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Chlorine and Hydrogen Chloride

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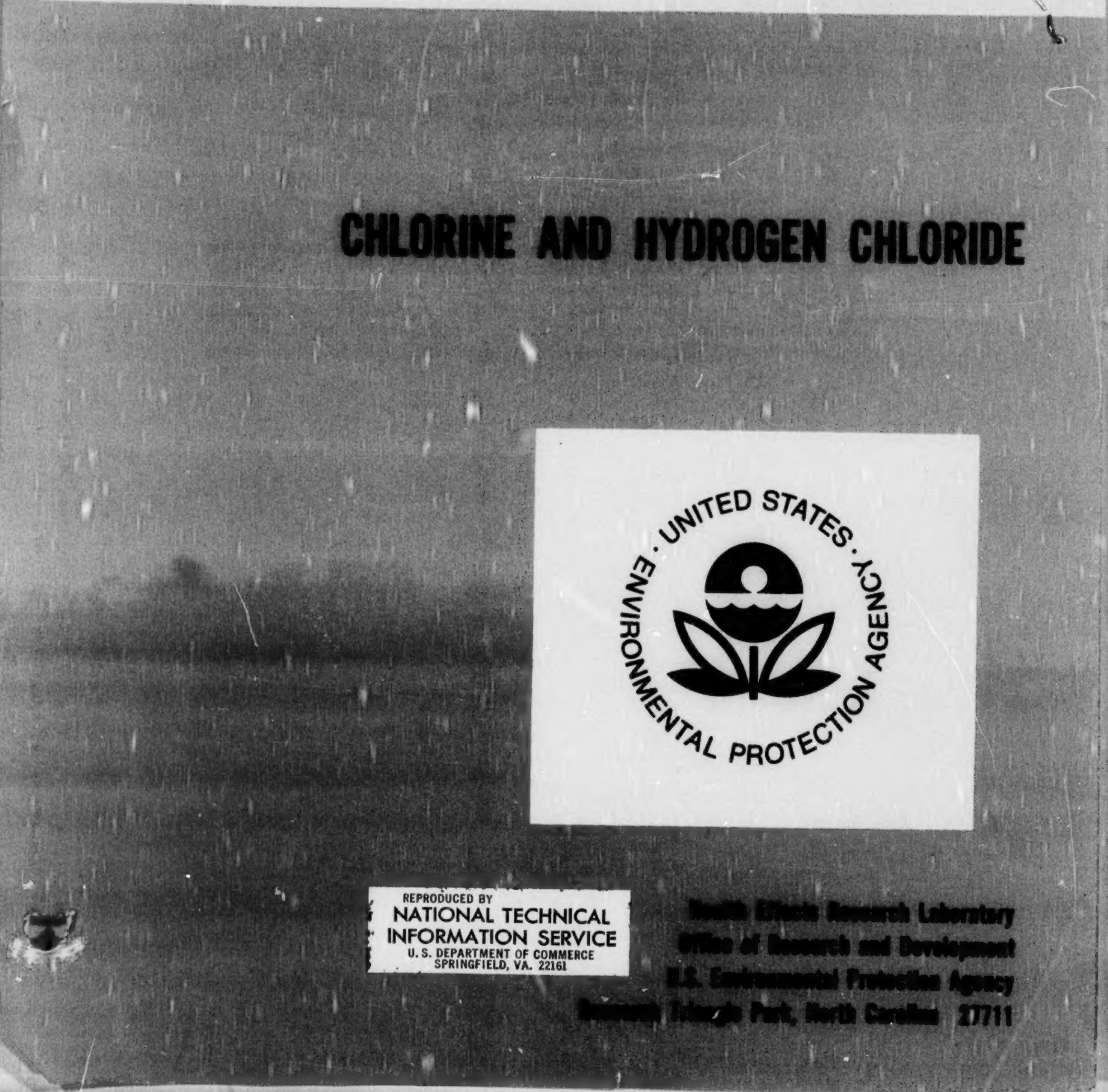
CHLORINE AND HYDROGEN CHLORIDE



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The purpose of this report is to discuss the medical, biologic, and environmental effects of chlorine pollution in the lower atmosphere. The first three chapters discuss the natural and anthropogenic sources of pollution by chlorine and hydrogen chloride, the varied industrial and other usages of chlorine and hydrogen chloride and the quantities consumed, the atmospheric chemistry of their transformation and transport processes, and their spatial distribution.

Later chapters deal with the effects of chlorine and hydrogen chloride on man, animals, vegetation, and materials. Chapters 9 and 10 present the summary and conclusions and offer recommendations for consideration in future studies. Methods of monitoring and analyzing aqueous, gaseous, and biologic samples for chlorine and hydrogen chloride are discussed in the Appendix.

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CHLORINE AND HYDROGEN CHLORIDE

By

Subcommittee on Chlorine and Hydrogen Chloride
National Academy of Sciences
National Research Council
Committee on Medical and Biologic Effects
of Environmental Pollutants
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U.S. ENVIRONMENTAL PROTECTION AGENCY
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The project that is the subject of this report was approved by the Governing Board of the National Research Council, whose members are drawn from the Councils of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine. The members of the Committee responsible for the report were chosen for their special competences and with regard for appropriate balance.

This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

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CHAPTER 1

INTRODUCTION

Each year, many millions of tons of chlorine are produced to meet the demands of the chemical industry and to satisfy the demand for chlorine in the purification of domestic water supplies. As a consequence of the manufacture and use of this element, some chlorine gas escapes to the atmosphere. In addition, the action of sunlight on chloride-containing aerosols has been shown to produce small amounts of chlorine. Occasionally, exposure of populations to high concentrations of chlorine has occurred, usually as a result of accidents involving the transportation of chlorine by rail, truck, or barge. For a brief time, during World War I, chlorine was intentionally used in warfare, although by most standards it was not a very effective weapon.

Hydrogen chloride is also an important basic chemical, and its close relationship to chlorine makes it desirable to consider the two substances together in discussing environmental effects.

The purpose of this report is to discuss the medical, biologic, and environmental effects of chlorine pollution in the lower atmosphere. The next three chapters discuss the natural and anthropogenic sources of pollution by chlorine and hydrogen chloride, the varied industrial and other usages of chlorine and hydrogen chloride and the quantities consumed, the atmospheric chemistry of their transformation and transport processes, and their spatial distribution.

Later chapters deal with the effects of chlorine and hydrogen chloride on man, animals, vegetation, and materials. Chapters 9 and 10 present the summary and conclusions and offer recommendations for consideration in future studies. Methods of monitoring and analyzing aqueous, gaseous, and biologic samples for chlorine and hydrogen chloride are discussed in the Appendix.

Unless stated otherwise, "chlorine" refers to the element and "hydrogen chloride" to the molecule HCl. "Gaseous chlorine" refers to the element when it is present as the diatomic molecule. It should be understood that gaseous chlorine and hydrogen chloride in the atmosphere are complexed with condensation nuclei of unspecified chemical composition.

A balance was sought in apportioning the representation of expertise and interests of industry and academe in studying the two chemicals in question. Each participant in the study was asked to prepare a section of the report based on a review and evaluation of the published information obtained from national and international sources that were available up to July 1, 1974. The summary, conclusions, and recommendations for each section were prepared by its author and these were consolidated to form Chapters 9 and 10. The drafts of individual chapters were reviewed and appropriately revised by members of the Subcommittee on Chlorine and Hydrogen Chloride. The complete manuscript was also approved by the Committee on Medical and Biologic Effects of Environmental Pollutants.

CHAPTER 2

SOURCES OF CHLORINE AND HYDROGEN CHLORIDE

CHLORINE AND HYDROGEN CHLORIDE IN THE ENVIRONMENT

Industrial production of chlorine in the United States has grown and continues to grow at a high rate. In 1972, 9,859,800 tons of chlorine were produced, compared with 5,142,876 tons in 1962 (an increase of about 6.7% per year), and production was projected to increase at the rate of approximately 7% per year through 1974.[77,98] The major commercial sources of chlorine are the electrolysis of water solutions of the alkali chlorides (96.6% of total installed U.S. production capacity in 1972) and the electrolysis of fused sodium chloride-calcium chloride salt mixture, in which chlorine is obtained as a by-product of sodium production (slightly under 3.4% of total installed U.S. capacity in 1972).[81] Because the largest users of chlorine are the chemical industry (approximately 70% of total consumption) and the pulp and paper industry (approximately 18% of total consumption,[77] the number of sources of possible chlorine emission tends to be restricted, compared, for example, to the number of sources of possible emission of the oxides of sulfur and nitrogen. Chlorine emission control is generally effective and has been in widespread use in industry for many years.

The 7.7% average annual growth in the industrial production of hydrochloric acid (100% basis*) in the United States over the period 1962-1972 has slightly outstripped the 6.7% average annual growth in the production of chlorine. In 1972, 2,198,140 tons of hydrochloric acid (100% basis) (22.3% of the chlorine tonnage) were produced, compared with 1,052,116 tons in 1962

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*"100% basis" means on the basis of equivalent anhydrous hydrogen chloride.

(20.5% of the chlorine tonnage).[98] Production of hydrochloric acid (100% basis) is projected to increase over the next few years at an average annual rate of approximately 5-7%.[234] In the United States, hydrogen chloride is produced by three major processes:[88] as a byproduct of the chlorination of organic compounds; by reaction of chloride salt with sulfuric acid (the Mannheim process) or with sulfur dioxide, steam (water), and air (oxygen)--the Hargreaves process--at high temperature to produce salt cake (sodium sulfate) and hydrogen chloride; and by reaction of chlorine with hydrogen gas. Only one large plant using the Hargreaves process is still in operation in the United States.[88] In common with chlorine production, industrial hydrogen chloride production is confined largely to a few chemical organizations that use one or more of the three major processes and that use an estimated 55-60% of the total production. Theoretically, the essentially anhydrous gaseous hydrogen chloride produced via the three routes (with chlorine, chlorinated organic compounds, other organic materials, and other chemicals in the gas stream) represents a significant atmospheric emission control problem. In practice, however, such potential emission is most commonly, effectively, and inexpensively controlled by scrubbing the main exit-gas stream and any tail-gas stream with water to produce hydrochloric acid for use, sale, or disposal; and other emission control systems have been developed to meet special industrial requirements.

The burning of huge amounts of chloride- or chlorine-containing fossil fuels--coal and fuel oil--is a very large source of emission of hydrogen chloride gas to the atmosphere. The magnitude of the problem is discussed further in the section on Combustion of Fuels.* Increasing effort is being directed toward the development of adequate and economical scrubber systems for

*Page 21

the control of emission of sulfur dioxide, nitrogen oxides, and hydrogen chloride from coal- and oil-fired industrial heating plants and electric generati plants, such systems are not now in general use in the United States.

The incineration of chloride- or chlorine-containing refuse, paper, and plastics (particularly polyvinylchloride) is another important source of emission of hydrogen chloride gas to the atmosphere. The magnitude of this source is also unknown and is being looked into.

There is evidence that hydrogen chloride gas is emitted to the atmosphere in the exhaust resulting from the combustion of hydrocarbon fuels in transportation. If it is emitted, data to determine its extent are not available. Hydrogen chloride from such a source would probably be in the form of hydrochloric acid aerosol because of the water present in exhaust. The only transportation fuel considered even potentially significant as a source of hydrogen chloride gas emission is motor gasoline that contains the ethylene dichloride scavenger used with lead antiknock compounds. The potential for hydrogen chloride gas emission from transportation sources will decrease significantly, as the EPA imposes regulations to decrease the lead content of gasoline.

The National Aeronautics and Space Administration (NASA) Office of Space Science (OSS) Launch Vehicle and Propulsion Programs, in a final environmental statement published in July 1973, indicated that, with respect to global or even national significance, the contribution of NASA launch vehicles for automated missions to environmental pollution appears to be much smaller than that of other sources.[355] The environmental effects of hydrogen chloride gas emitted from rocket engines in tests, launches, on-pad accidents, and inflight abort situations have been considered.

Concentrations of hydrogen chloride gas in the ambient atmosphere have not been reported. Under normal atmospheric conditions, hydrogen chloride is an aqueous acid aerosol; usually low relative humidity may allow it to exist as anhydrous hydrogen chloride.[356] There has been one report of hydrochloric acid aerosol concentrations in the atmospheric air near a Russian magnesium plant.[126] Studies of hydrochloric acid aerosol concentrations in atmospheric air have undoubtedly been hindered because of the unavailability of an analytic method with high specificity for hydrogen chloride itself. Most analytic methods for hydrogen chloride are based on its acidity or on total-chloride determination, and these conventional methods are subject to interferences from other contaminants commonly found in atmospheric air (see the Appendix).

Determinations of background concentrations of chlorine in the ambient atmosphere have not been reported. The air in a 6-square-mile area around a 1961 chlorine tank-car derailment in Louisiana was sampled for chlorine emission.[253]

NATURAL SOURCES OF CHLORINE AND HYDROGEN CHLORIDE

Minute quantities of hydrogen chloride gas are present in volcanic gases,[276] but it is readily converted to hydrochloric acid aerosol by the moisture in the air.

All human body fluids contain chlorine: blood at 0.45% (expressed as sodium chloride) and gastric juices at 0.4-0.5% (as hydrochloric acid).[461a]

The formation of hydrochloric acid in the gastric juices is closely associated with the parietal cells of the gastric glands; one accepted theory is that the hydrochloric acid forms in the absence of carbonates as a result of the interchange of ions between sodium chloride and carbonic acid.[36] Nothing in the literature suggests that emission of chlorine or hydrogen chloride gas to the atmosphere results from biochemical reactions; it is extremely unlikely that chlorine or hydrogen chloride gas can be emitted to the atmosphere as a result of biochemical reactions.

Chlorine at low concentrations may be formed by atmospheric reactions.[266] For example, chloride compounds and nitrogen dioxide may react to form nitrosyl chloride, which can decompose photochemically to yield free chlorine and nitric oxide. Free chlorine may also be formed in the atmosphere by the reaction of chloride ion and ozone.*

It is pointed out in Chapter 4 that there is considerable circumstantial evidence (measurements of the chloride:sodium ratio in the atmosphere in West Coast cities) that sea salt particles (sodium chloride) in the presence of moisture undergo attack by acid-forming gases, such as nitrogen dioxide, to release hydrogen chloride gas. In urban areas, where concentrations of nitrogen dioxide may be relatively high, the chloride:sodium ratio is much lower than would be expected if it were reduced by addition of only soil dust to the sea salt aerosol. See Chapter 4 regarding this an other possible atmospheric reactions leading to the formation of hydrogen chloride gas.

*See also page 103

ARTIFICIAL SOURCES OF CHLORINE AND HYDROGEN CHLORIDE

Manufacture

Chlorine. The major processes for the production of chlorine in the United States are the electrolysis of water solutions of alkali chlorides via diaphragm or mercury cells and (to a much smaller extent) the electrolysis of a fused sodium chloride-calcium chloride mixture (Downs process). Other processes used for the production of chlorine include the electrolysis of magnesium chloride fused with other chlorides,[319] the electrolysis of hydrochloric acid,[85] and a process wherein chlorine is obtained as a byproduct of the reaction of potassium chloride with nitric acid and oxygen to form potassium nitrate.[87] Those three processes together account for only approximately 0.1% of chlorine production and details on them in the literature are sparse.

Diaphragm- and mercury-cell processes accounted for approximately 96.6% of the chlorine produced in 1972 (about 72.4% and 24.2%, respectively).[81] Detailed descriptions of these processes can be found in several reference sources.[87,200,415,480] Slightly under 3.4% of the chlorine manufactured in this country is produced as a byproduct of the Downs fused-salt process.[81,87]

There were 68 plants producing chlorine in the United States in 1972; they are listed in Table 2-1, with the type of process used, the year of initial chlorine production, and the kinds of containers filled.

The major sources of atmospheric emission of chlorine from the production processes are the blow gas resulting from the liquefaction of chlorine; the vents from returned tank cars, ton containers, and cylinders; the vents from storage tanks, process transfer tanks, and tank cars during handling and storage of liquid chlorine; the process for the removal of water from chlorine gas; emergency vents; the air blowing of depleted brine in mercury-cell plants; and occasional equipment failure (especially compressor breakdown).[87]

TABLE 2-1

CHLORINE PLANTS IN THE UNITED STATES[a]

Location	Producer	Year Chlorine Production Began	Cells	Containers Filled[b]
Alabama				
Le Moyne[c]	Stauffer Chemical Company	1965	De Nora 22 x 5 (merc.)	- - S B
McIntosh[c]	Olin Corporation	1952	Olin E8 (merc.)	- - S B
Mobile[c]	Diamond Shamrock Chemical Co.	1964	De Nora (merc.)	- - S -
Muscle Shoals[d]	Diamond Shamrock Chemical Co.	1952	De Nora 24 x 2M (merc.)	- - S B
Arkansas				
Pine Bluff[e]	U.S. government	1943	Hooker S (diaph.)	
California				
Pittsburg[c]	The Dow Chemical Company	1917	Dow (diaph.)	- T S -
Delaware				
Delaware City[d]	Diamond Shamrock Chemical Co.	1965	De Nora 18 x 4 (merc.)	- - S -
Georgia				
Augusta[c]	Olin Corporation	1965	Olin E11F (merc.)	- - S -
Brunswick[c]	Allied Chemical Corp.	1957	Solvay V-100 (merc.)	- - S -
Brunswick[c,f]	Brunswick Chemical Co.	1967	Hooker S4 (diaph.)	- - - -
Illinois				
East St. Louis[d]	Monsanto Company	1922	De Nora 18 x 6 (merc.)('62)	- - S -
Kansas				
Wichita[c]	Vulcan Materials Co.	1952	Hooker S,S3A,S3B (diaph.)	C T S -
Kentucky				
Calvert City[c]	B.F. Goodrich Chemical Corp.	1966	De Nora 24H5 (merc.)	- - - -
Calvert City[d]	Pennwalt Corp.	1953	Olin E11F (merc.)('67)	- - S B
Louisiana				
Baton Rouge[c,g]	Ethyl Corporation	1938	Downs (fused salt), Hooker S3D (diaph.)	- - S -
Baton Rouge[c]	Allied Chemical Corp.	1937	Allen-Moore (modified diaph.), Hooker S4 (diaph.)('68)	- - S -
Geismar[c]	BASF Wyandotte Corp.	1959	Diamond D3 (diaph.), Uhde 30 sq. m. (merc.)('64), Hooker S4 (diaph.)('69)	- - S B

TABLE 2-1

CHLORINE PLANTS IN THE UNITED STATES[a] - (Cont'd)

Location	Producer	Year Chlorine Production Began	Cells	Containers Filled[b]
Gramercy[c]	Kaiser Aluminum & Chemical Corp.	1958	Hooker S3B (diaph.)	- - S B
Lake Charles[c]	PPG Industries, Inc.	1947	Columbia N 1, Hooker S3B (diaph.), De Nora 48H5 (merc.)('69)	- T S B
Plaquemine[c]	The Dow Chemical Company	1958	Dow (diaph.)	- - S -
St. Gabriel[c]	Stauffer Chemical Company	1970	Uhde 30 sq. m. (merc.)	- - S B
Taft[c]	Hooker Chemical Corp.	1966	Hooker S4, C-60, H-2 (diaph.)	- - S -
Maine				
Orrington[c]	Sobin Chlor-Alkali Inc.	1967	De Nora 24H5 (merc.)	- - S -
Michigan				
Midland[c]	The Dow Chemical Company	1897	Dow (diaph.)	- - S -
Montague[c]	Hooker Chemical Corp.	1954	Hooker HC-3 (diaph.)	- - S -
Wyandotte[c]	BASF Wyandotte Corp.	1938	Hooker S3B (diaph.)	- - S -
Wyandotte[c]	Pennwalt Corp.	1898	Diamond D3 (diaph.)('60)	C T S -
Mississippi				
Vicksburg[h]	Vicksburg Chemical Co.	1962	None	- - S -
Nevada				
Henderson[c]	Stauffer Chemical Co. of Nevada Inc.	1942	Hooker S (diaph.)	- - S -
New Jersey				
Linden[c]	Linden Chlorine Products Inc.	1956	BASF-Krebs ('69)	- T S -
Newark[c]	Vulcan Materials Co.	1961	Hooker S (diaph.), Hooker S4 ('68)	- - S -
New York				
Niagara Falls[g]	E.I. du Pont de Nemours & Co. Inc.	1898	Downs (fused salt)	- - - -
Niagara Falls[d]	Hooker Chemical Corp.	1898	Hooker S,S3A, Gibbs (modified diaph.)('61)	- T S -

TABLE 2-1

CHLORINE PLANTS IN THE UNITED STATES[a] - (Cont'd)

Location	Producer	Year Chlorine Production Began	Cells	Containers Filled[b]
Niagara Falls[i]	Hooker Sobin Chemical	1971	Uhde 20 sq. m. (merc.)	- - S -
Niagara Falls[c]	Olin Corporation	1897	Olin E11F (merc.)('60)	- - S -
Syracuse[d]	Allied Chemical Corp.	1927	Allen-Moore (modified diaph.), Solvay Process SD 12 (merc.)('46), Solvay S60 (merc.) ('53), Hooker S4 (diaph.) ('68)	
North Carolina				
Acme[c]	Allied Chemical Corp.	1963	Solvay V-200 (merc.)	- - S -
Canton[c,f]	Champion International Corp.	1916	Hooker S (diaph.)	- - - -
Pisgah Forest[c,f]	Olin, Ecusta Operations	1947	Sorensen (merc.)	- - - -
Ohio				
Ashtabula[c]	Detrex Chemical Industries, Inc.	1963	Olin E11F (merc.)	- - S -
Ashtabula[g]	RMI Company	1949	Downs (fused salt)	- - S -
Barberton[c]	PPG Industries Inc.	1936	Columbia (diaph.)	- T S -
Painesville[c]	Diamond Shamrock Chemical Co.	1928	Diamond D3 (diaph.)('59)	C T S -
Oregon				
Albany[j]	Oregon Metallurgical Co.	1970	Alcan (magnesium)	- - - -
Portland[c]	Pennwalt Corp.	1947	Gibbs, Gibbs (modified diaph.), Diamond (diaph.)('67)	C T S B
Tennessee				
Charleston[c]	Olin Corporation	1962	Olin E11F, E812 (merc.)	- - S B
Memphis[g]	E.I. du Pont de Nemours & Co. Inc.	1958	Downs (fused salt)	- - S -
Memphis[c]	Velsicol Chemical Corp.	1943	Hooker S4 (diaph.)('69)	- - S -
Texas				
Cedar Bayou[k]	Mobay Chemical Co.	1972	Uhde (HCI)	- - - -
Corpus Christi[d]	PPG Industries, Inc.	1938	Columbia N 1, N 3 (diaph.)	- T S -
Denver City[c]	Vulcan Materials Co.	1947	Hooker S (diaph.)	- - - -
Freeport[c,j,l]	The Dow Chemical Co.	1940	Dow (diaph.), Dow (magnesium)	- - S -
Deer Park[d]	Diamond Shamrock Chemical Co.	1938	Diamond (diaph.), De Nora 18 SGL (merc.)	C T S B

TABLE 2-1

CHLORINE PLANTS IN THE UNITED STATES[a] - (Cont'd)

Location	Producer	Year Chlorine Production Began	Cells	Containers Filled[b]
Houston[g]	Ethyl Corporation	1952	Downs (fused salt)	- - S -
Houston[c]	Shell Chemical Co.	1966	Hooker S4 (diaph.)	- - - -
Houston[c,f]	Champion International Corp.	1936	Hooker S (diaph.)	- - - -
Point Comfort[c]	Aluminum Co. of America	1966	De Nora 24 x 5 (merc.)	- - S B
Port Neches[c]	Jefferson Chemical Co., Inc.	1959	Hooker S3B (diaph.)	- - - -
Snyder[e,j]	American Magnesium Co.	1969	VAMI (magnesium)	- - - -
Virginia				
Hopewell[c]	Hercules, Inc.	1939	Hooker S3 (diaph.)	- - S -
Washington				
Bellingham[c,f]	Georgia-Pacific Corp.	1965	De Nora 18 x 4 (merc.)	- - S B
Longview[c,f]	Weyerhaeuser Company	1957	De Nora 14 TGL & 24H5 (merc.)('67)	- - S -
Tacoma[c]	Hooker Chemical Corp.	1929	Hooker S3 (diaph.)	- T S B
Tacoma[c]	Pennwalt Corp.	1929	Gibbs (modified diaph.)	C T S -
West Virginia				
Moundsville[c]	Allied Chemical Corp.	1953	Solvay S60 (merc.)	- - S B
New Martinsville[c]	PPG Industries Inc.	1943	Columbia N 1, N 3, N 6 (diaph.), Uhde 20 sq. m. (merc.)('58)	- - S B
So. Charleston[c]	FMC Corporation	1916	Hooker S3B (diaph.)('57), Hooker S4 (diaph.)('67)	- T S B
Wisconsin				
Green Bay[c,f]	Fort Howard Paper Co.	1968	Hooker S4 (diaph.)	- - - -
Port Edwards[c]	BASF Wyandotte Corp.	1967	De Nora 24H5 (merc.)	- - S -
PUERTO RICO				
Guayanilla[c]	PPG Industries (Caribe)	1971	De Nora (merc.)	- - - -

TABLE 2-1

CHLORINE PLANTS IN THE UNITED STATES - (Footnotes)

[a] Derived from Chlorine Institute;[81] excludes plants being built.

[b] C=cylinders, T=ton containers, S=single-unit tank cars, B=barges.

[c] Electrolytic plant producing caustic soda, chlorine, and hydrogen from brine.

[d] Electrolytic plant producing caustic soda, caustic potash, chlorine, and hydrogen from brine.

[e] Not operating.

[f] Pulp mill.

[g] Electrolytic plant producing metallic sodium and chlorine from molten salt.

[h] Nonelectrolytic plant producing chlorine and potassium nitrate.

[i] Electrolytic plant producing caustic potash, chlorine, and hydrogen from brine.

[j] Electrolytic plant producing magnesium and chlorine from molten magnesium chloride.

[k] Electrolytic plant producing chlorine and hydrogen from hydrochloric acid.

[l] Includes both Texas and Oyster Creek divisions.

Chlorine and caustic are produced concurrently in electrolytic diaphragm and mercury cells. An electric current decomposes a chloride salt that is fed to the cell as a water solution. Chlorine gas is liberated at the anode of the cell. In the diaphragm cell, hydrogen is liberated at the cathode, and a diaphragm is used to prevent contact of the chlorine that is produced with the hydrogen or alkali hydroxide that is formed simultaneously. In the mercury cell, liquid mercury is used as the cathode and forms an amalgam with the alkali metal. The amalgam is removed from the cell and reacted with water in a separate chamber, called a denuder, to form alkali hydroxide and hydrogen.

Both chlorine and hydrogen are produced in the electrolytic diaphragm and mercury cells. Hydrogen gas saturated with water vapor leaves the cell at the top of the cathode or denuder compartment. Chlorine gas leaving the cells from the anode compartment is saturated with water vapor and is cooled to remove some of the water. In the operation of the diaphragm cell, cooling may be indirect or by direct contact with cold water, as in a blow-gas absorber. Chlorine gas from mercury cells is usually cooled indirectly with cold water. After water cooling, the gas is dried further by direct contact with strong sulfuric acid. The dry chlorine gas is then compressed for in-plant use or refrigerated to liquefy it. Approximately half of the chlorine produced in the United States is produced as a liquid.

Electrolysis of a fused sodium chloride-calcium chloride mixture occurs in the Downs cell at a temperature of about 550 C, producing molten elemental sodium and gaseous chlorine. The lower-density sodium and the chlorine percolate separately through the molten salt bath to a submerged conical collection dome, where an outer annulus and an inner nickel dome remove the molten sodium and hot gaseous chlorine. The chlorine is cooled indirectly and then handled by methods similar to those used in association with diaphragm and mercury cells.

The potential emissions are described in the following paragraphs.

Gaseous chlorine is present in the blow gas resulting from the liquefaction of chlorine. The chlorine content of blow-gas streams normally ranges from 20 to 100 lb/ton of chlorine produced with diaphragm cells and from 40 to 160 lb/ton of chlorine produced with mercury cells.[87] Methods of removing chlorine from these streams are summarized later in this Chapter.

It is common practice to apply suction to returned tank cars, ton containers, and cylinders to remove liquid chlorine remaining in the vessels before inspection and cleaning. The amount of chlorine thus removed varies considerably, but averages about 450 lb for a 55-ton tank car (or about 8 lb/ton of carrying capacity).[87] The recovered chlorine from tank cars is usually sent to the operating system for process chlorine handling, but plants find it convenient to send minor quantities of chlorine to a caustic scrubber to avoid upsetting their operating systems.

A common method of transferring chlorine involves the use of air padding.* After transfer, it is necessary to vent the air, which now contains a relatively low concentration of chlorine, because the transfer is normally completed before equilibrium can be reached. Data from 19 plants (in response to a questionnaire for a study) show that the quantity of chlorine flushed out with the padding air during the loading of shipping containers with liquid chlorine varied from 1.1 to 60 lb/ton of chlorine liquefied, with an average of 17 lb.[87] The chlorine removed during tank-car loading is transferred to other plant uses, returned to the process, or treated in a scrubber. In many newer plants, submerged pumps are used to transfer liquid chlorine. Although pumps eliminate the loss of chlorine related to padding, emergency venting (usually to a caustic scrubber) is necessary for pump repair and general maintenance.[87] Another method of transfer is to apply suction on the receiver or vessel to which a transfer is to be made and connect the discharge from the compressor to the vessel that contains the chlorine to be transferred. This is somewhat similar to transfer by air, except that neither tank requires any venting.[87]

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*Use of compressed air above the surface of a liquid to transfer the liquid to another vessel.

Chlorine gas is normally cooled to condense water vapor and then dried further in scrubbers with concentrated sulfuric acid. The potential loss of chlorine with the water that condenses from cell gas varies from 4 to 12 lb/ton liquefied and depends on the type of cell, cell temperature, and location of drip connections in the chlorine gas system.[87] In modern practice, the water that condenses can be passed to the plant water collection system through a limestone pit[480] or acidified and steam-stripped to a chlorine content of less than 10 ppm (0.1-0.2 lb of chlorine per ton liquefied) in a process vessel before disposal. Chlorine stripped from the water condensate is recovered by piping it back to the cell-gas stream ahead of the first indirect-contact cooler.

Chlorine seals and other sources of infrequent emission are usually connected to an emergency scrubber, although in other cases such emission is vented to the atmosphere. In either event, alarms and electric tie-in connections are usually provided to permit prompt shutdown or changes in operating procedures to limit the duration of the emission.[87] Seals on chlorine headers, provided to prevent back-pressure at the cells, commonly used to be vented to the cell house or to the atmosphere. Although in an emergency they must handle the full capacity of the cells connected to the header, the seals blow only infrequently and for short periods.[87] Modern practice is to pipe the seals to a lime or caustic scrubber designed to absorb all the cell chlorine produced. The shaft seals on liquid-seal chlorine compressors are usually piped so that a stream of sulfuric acid is fed into the compressor. Carbon-ring reciprocal compressors usually have a double stuffing box vented to a caustic scrubber or the suction of the compressor. This effectively prevents emission to the atmosphere.[87] Storage-tank vent lines are usually connected to a disposal scrubber. The relief connection from the safety valves may be vented to the atmosphere or to an emergency scrubber.[87]

Recycled brine in mercury-cell plants is saturated with chlorine. This brine is usually vacuum-treated, air-blown, or both, to remove residual chlorine before resaturation. Concentrations of chlorine encountered in the vent gas are usually low, and recovery in a water or carbon tetrachloride absorber is not economical. Consequently, such gases are normally used for in-plant purposes, such as water chlorination, or are sent to lime or caustic scrubbers for disposal or vented to the atmosphere. Although air-blowing of depleted brine is common, it is by no means universal. For example, some plants air-blow and re-treat only a 5-10% sidestream, and several plants dispense with this procedure entirely. The questionnaire responses indicated that 11 plants treat depleted brine by air-blowing: seven use the recovered chlorine for in-plant processes, three send it to scrubbers, and one vents it to the atmosphere.[87]

Minor emission of chlorine in cell rooms can lead to emission to the atmosphere. In the operation of diaphragm cells, this results from leakage at dogleg connections (those between the cell and the main chlorine header) due to improper assembly or overpressure at the cell and from cell renewal. Modern control techniques and developments include operation at a slight negative pressure (approximately 0.5 in. H_2O gauge) in the chlorine header, the elimination of packed joints in dogleg assemblies through improved design, and essentially complete draining of chlorine-containing brine from the cells into the caustic system before cell renewal. In some mercury cells, the discharge end box has a removable cover for servicing. End boxes are connected to a common suction header to prevent chlorine gas from entering the cell room when the covers of the end boxes are opened. Chlorine exhausted from the end boxes is usually neutralized with lime or caustic in a scrubber system.[87]

Hydrogen Chloride. In 1972, 90% of the hydrochloric acid (100% basis) produced in the United States was manufactured as a byproduct of the chlorination of organic compounds.[98] Byproduct hydrogen chloride is produced in the manufacture of chlorinated benzenes, chlorinated toluenes, vinylchloride, fluorocarbons, carbon tetrachloride, toluene diisocyanate, glycerin, linear alkylsulfonate detergents, chloroform, methylene chloride, methylchloride, trichloroethylene, perchloroethylene, chloral, hexachlorocyclopentadiene, chlorinated paraffins, ethylchloride, and other substances.[190, 227, 276] Thus, hydrogen chloride is a byproduct in any manufacturing process in which chlorine is used to substitute a chlorine atom for hydrogen in a chemical compound. Hydrogen chloride also is produced as a byproduct when a saturated chlorinated compound is dehydrochlorinated to produce an unsaturated compound that contains one less chlorine atom than the saturated chlorinated compound precursor. Hydrochloric acid is produced from byproduct process hydrogen chloride by absorbing the hydrogen chloride in water after the organic materials associated with it are removed by condensation, absorption, or adsorption. The atmospheric contaminants that can be emitted during the manufacture of hydrochloric acid from byproduct process hydrogen chloride include hydrogen chloride, chlorine, chlorinated organic compounds, and other organic materials. The type and quantity of contaminants vary with the type of process, the operating conditions, and the type of exit-gas control systems.

In a cooperative study report[88] of the Manufacturing Chemists' Association, Inc., and the Public Health Service, published in 1969, hydrogen chloride emission data and data on other trace emission from byproduct plants were obtained from 17 plants by questionnaire. In addition, hydrogen chloride-containing stack gases from four other byproduct plants were sampled by a Public Health Service team as part of the overall cooperative study project. It was concluded in the cooperative study that hydrogen chloride emission to the atmosphere usually totals less that 0. 5% of the tail-gas volume. This is a relatively small quantity of hydrogen chloride; tail-gas volumes for plants reporting range from 2 to 550 cfm, with an average of 40 cfm.

Adequate control equipment is available to prevent emission of more than 0. 5% hydrogen chloride, or about 0. 5 lb/ton of acid produced.

In the event of an emergency shutdown of a hydrochloric acid plant (producing acid by absorbing hydrogen chloride gas in water), the hydrogen chloride gas source should be shut down first. Liquid flow to the absorption equipment should always be sufficient to keep all tubes or packing wetted and thus prevent hydrogen chloride emission to the atmosphere. Some weak acid will be made during this shutdown period, but that can usually be corrected by producing acid somewhat stronger than normal later. The liquid flow should be greater than that required for surface wetting, to prevent hydrogen chloride emission during routine shutdowns and startups.

In a survey[2] prepared for the Office of Air Programs of the Environmental Protection Agency and reported in 1972, 25 chlorination processes involved in production of 14 organic chemical products (one containing no chlorine) and two chlorine-containing inorganic chemicals (phosgene and synthesis hydrogen chloride) were examined to determine their air pollution potential. The manufacture of the selected 14 organic chemical products consumed 64. 3% of the chlorine produced in 1970. Excluding the two inorganic chemical chlorination processes and five organic chemical chlorination processes that produce no hydrochloric acid byproduct, 10 of the remaining 18 chlorination processes that did produce hydrochloric acid byproduct were listed as having no hydrogen chloride emission factor (pounds of hydrogen chloride emitted per ton of product). Emission factors for the other eight chlorination processes were 0.001 (for three processes: chlorination of ethylene, chlorination of benzene, and hydrochlorination of ethylene), 0.002 (for two processes: chlorohydrination of allylchloride and then hydrolysis and chlorohydrination of propylene and then hydrolysis), 0.02 (for one process: hydrochlorination of ethanol), and 0.2 (for two processes: dehydrochlorination of 1,2-dichloroethane and chlorination and then dehydrochlorination of acetylene). With one insignificant exception, the emission factors were estimated on the basis of little or no census or experimental information and are averages for all sources using the processes in question.

The synthesis process[88] accounted for 5.6% of the hydrochloric acid (100% basis) produced in 1972.[98] In this process, high-purity (98-99.7% pure) hydrogen chloride gas is produced by burning chlorine in a slight excess of hydrogen.[201] The high-purity gas is desirable for organic compound or drug synthesis and the manufacture of reagent-grade acid. Synthesis plants differ in detail, because of differences in raw-material sources and qualities and plant capacity. However, all plants have a chlorine burner, including safety and control devices, and absorption facilities for the production of hydrochloric acid. Hydrogen chloride formed in the combustion chamber can be cooled and absorbed in water or cooled, dried with sulfuric acid, and compressed for pipeline distribution. Some plants liquefy dried synthesis-process hydrogen chloride and revaporize the liquid to meet fluctuations in captive and merchant sale demands. In the cooperative study project of the Manufacturing Chemists' Association, Inc., and the Public Health Service, hydrogen chloride emission data from three synthesis plants were obtained in response to questionnaries,[88] and emission factors--pounds of hydrogen chloride emitted per ton of 20 Bé (Baumé) /(31.5% acid)--of zero, trace, and < 0.035 were reported. In the plants surveyed, no additional air pollution control equipment was used after the tail-gas (lean-gas) absorption tower. In the survey prepared for the Office of Air Programs of the EPA, an emission factor of 0.1 was reported for the hydrogen chloride synthesis process.[2] According to the survey report, that emission factor was estimated on the basis of little or no census or experimental information and is an average for all sources using the synthesis process.

In 1972, 4.4% of the hydrochloric acid (100% basis) manufactured in the United States was produced by the reaction of sulfuric acid with sodium chloride (Mannheim process) or by the reaction of sulfur dioxide, steam (water), air (oxygen), and sodium chloride (Hargreaves process).[98] The Mannheim process is operated at about 1000 F and the Hargreaves process at 800-1000 F, to produce hydrochloric acid and a salt cake (sodium sulfate) coproduct.[276] In addition to hydrogen chloride gas, both sulfuric and hydrochloric acid mists are emitted from Mannheim process plants. In general, emission from such plants is greater than that from byproduct or synthesis-process plants. Data reported by manufacturers and collected by actual test showed hydrogen chloride emission factors of 1.3-3.8 lb/ton of 20 Bé acid produced. These factors are probably higher because of poor operation and maintenance and, in some cases, poor design of absorption systems.[88] In the Mannheim furnace operations, losses of hydrogen chloride can also occur through leaks at the furnace and through removal of hot salt cake.[201] No quantitative data are available on the magnitude of such losses to the atmosphere from the Hargreaves process.

Combustion of Fuels

The combustion of fossil fuels, particularly coal, produces a major contribution to the chloride content of the atmosphere. In one recent study,[307] it was concluded that high concentrations of chloride occur in areas of heavy industrialization and that this chloride is generated largely by combustion of fuels. This is confirmed by seasonal variations, which show high concentrations during the winter months in urban areas. The chloride:sodium ion ratio of seawater is about 1.8:1, and a map of the United States giving average ratios for the years 1960-1966 shows very high values in industrialized areas, indicating anthropogenic sources of chloride ion.

A literature review conducted under a Public Health Service contract[447] cited 11 references pertaining to the prevalence of chlorine in coal and its emission as hydrogen chloride during coal-burning. In a reference not cited in the literature review, Gibson and Selvig[163] indicated that tests on 24 coal samples from 12 states yielded chlorine content of 0-0.46%, with a mean of 0.128%. In one key reference cited in the literature review, Iapalucci *et al.*[237] concluded that the chlorine content of American coal ranges from 0.01 to 0.5% and that the burning of coal containing chlorine is associated with a serious pollution hazard. They assumed that an 800-MW power plant is burning coal with 0.2% chlorine and concluded that hydrogen chloride is discharged from the stack at 11,000 scf/hr, or 4,560 tons/year. They performed experiments with pulverized coal containing 0.1-0.4% chlorine at carbon combustion efficiencies of 94-98% and found that 93-98% of the chlorine was emitted as hydrogen chloride; the remainder was left in the ash. To verify these results under actual conditions, they sampled the stack of a local power plant after burning a bituminous coal containing 0.087% chlorine; only 1.5% of the chlorine was retained in the ash, with the balance being emitted in the stack gas as hydrogen chloride.

We consumed 1,053 billion pounds of coal (largely bituminous) in the United States in 1970, and it is estimated that we will consume 1,230 billion pounds of coal in 1975.[488] The data of Iapalucci et al. can be used in estimating the potential hydrogen chloride emission from coal-burning. For example, if it is assumed that the average chlorine content of coal is 0.128% and that 95% of it is converted to hydrogen chloride, then approximately 1.28 billion pounds of hydrogen chloride gas were emitted to the atmosphere from the burning of coal in the United States in 1970.

No supplementary quantitative literature references have been found regarding hydrogen chloride emission during coal-burning.

Fuel oil contains small amounts of chlorine and can therefore emit hydrogen chloride when burned. Few pertinent literature references are available, but a study on fuel-oil combustion published in 1962[440] cited two 1938 reports on chloride emission. It has been reported that 500 lb of hydrogen chloride are produced per day per 100,000 persons by using oil for domestic heating.[128]

Increasing effort is being directed toward the development of adequate and economical scrubber systems for the control of emission of sulfur dioxide, nitrogen oxides, and hydrogen chloride from coal- and oil-fired industrial heating plants and electric generating plants, but such systems are not now in general use in the United States.

Waste Disposal

"Incineration of refuse always produces at least two waste products, residue and combustion gases. Except for low "burnout" of the refuse, the residue is usually not a significant disposal problem because it is low in volume, sterile, and its offensive odors have been removed.... The combustion gases, however, can be a significant problem because of their contribution to air pollution. The primary air pollution concern is with particulate emissions rather than gases and odors..... air pollution control devices are basically designed for the removal of particulate matter, with some incidental removal of pollutant gases...."[449] The above comments indicate that concern over the control of incinerator combustion gases is a recent development in the United States. The primary reason is that, compared with other sources, incinerators contribute relatively little gaseous emission. In November 1965, 267 incinerators that burned municipal refuse in the United States were identified.[452] They had a nominal rated capacity of 76,300 tons/day (approximately 28 million tons/year). Projections of municipal incinerator capacity show an increase from the 1970 capacity of approximately 82,000 tons/day (approximately 30 million tons/year) to about 160,000 tons/day (approximately 58 million tons/year) in 1980.[21]

Results published in 1968 of the first national survey of solid wastes--made by representatives of the Solid Wastes Program of the Public Health Service, state agencies, and consultants--show that approximately 5.32 lb of municipal solid waste per person per day is collected.[40] The survey, based on a large sample consisting of 92.5 million people (46% of the U.S. population) in 33 states, permits the calculation of a national municipal solid waste collection figure of approximately 195 million tons/year. In the survey, projections on a national scale showed that the amount of solid wastes to be collected through municipal and private agencies will rise to 8 lb per person per day by 1980. The per capita projection coupled with the population projection would permit daily refuse disposal requirements to be projected.

The EPA has estimated that the municipal solid waste collected in 1967 was disposed of by municipal systems that included incineration (10%), open burning (44%), and other (46%); "other" included sanitary landfill, ocean dumping, and composting.[491] Another source has estimated sanitary landfill at 10% and incineration at 9-12%, unregulated dumping representing the balance.[222]

For the purpose of estimating control costs and emission reduction efficiencies in 1977, EPA said that all open burning in existing municipal systems would be discontinued by 1977, with 25% of the waste that is now being burned openly going to new municipal incinerators and 75% to sanitary landfills.

One incinerator emission that is generating a great deal of concern is that of hydrogen chloride gas from the combustion of chlorine- and chloride-containing refuse. Kaiser and Carotti[261] corroborated previous findings that hydrogen chloride is generated by burning normal refuse (e.g., paper, salt in food, grass, wool, leather, etc.) without the presence of plastics. During burning, most of the chlorine present in the normal refuse and in the polyurethane and polyvinylchloride materials added to the base refuse in the test work was evolved as hydrogen chloride. No free chlorine gas or phosgene was detected. The chloride ion concentration in the flue gas after the burning of the normal base refuse averaged 511 ppm (0.0511%).

Although analysis of paper products indicates that the chloride content is low,[35,47] approximately 0.03-0.16 wt %, two examples[47] cited in the literature demonstrate that the amount of hydrogen chloride emitted from the incineration of paper can injure plants. In both examples, the plant injury was caused by hydrogen chloride emitted from a hospital incinerator burning trash consisting of 80-90% paper products.

It is the presence of chlorine-containing plastics, however, and especially polyvinylchloride plastics, in the solid municipal refuse fed to incinerators that has become a concern of ecologically minded persons. That is because polyvinylchloride and polyvinylidene chloride plastics differ from most other plastic materials involved, in that they generate hydrogen chloride on incineration. In Kaiser and Carotti's study,[261] for example, addition of polyethylene and polystyrene plastics to normal base refuse (without plastics initially) had no effect on chloride ion emission, because they contain no chlorine. Addition of polyurethane foam resulted in slight increases, to 689 ppm (0.0689%) for a 2% addition to the base refuse and 751 ppm (0.0751%) for a 4% addition. Addition of polyvinylchloride to the normal refuse increased chloride ion emission to 1,990 ppm (0.1990%) for a 2% addition and 3,030 ppm (0.3030%) for a 4% addition.

Truss[482] indicates that the combustion of pure polyvinylchloride produces hydrogen chloride at about 58 wt % in the resulting combustion gas and is an important source of the hydrogen chloride that results from refuse incineration. Eberhardt,[124] in discussing European practice in refuse incineration, indicates that the chlorine content of polyvinylchloride in household refuse is about 50% and that, when the polyvinylchloride is heated to over 446 F, the chlorine appears as hydrochloric acid. Reimer and Rossi[393] in Hamburg, found a linear relationship between the amount of hydrogen chloride in an incinerator flue gas and the amount of polyvinylchloride added to the chloride-containing refuse for test purposes. For example, at a 4% polyvinylchloride in the refuse, the hydrogen chloride content of the flue gas was 4,000 mg/scm compared with 10,500 mg/scm at 9% polyvinylchloride. An approximately linear relationship was also found between the concentration of chlorides in the fly ash and the amount of polyvinylchloride added to the refuse for test purposes. With 3.5% polyvinylchloride in the feed refuse, the fly ash chloride concentration was about 3%; with 9% polyvinylchloride, the fly ash chloride concentration was 6.5%. In contrast, the chloride content of the slag, which ranged between 0.28 and 0.37% over the whole range of polyvinylchloride additions, was little affected by the polyvinylchloride content of the refuse. The latter observation is consonant with the belief that, at the actual temperatures of incineration, the chloride-containing materials also decompose, to give gaseous hydrogen chloride, which must either be reacted with the fly ash or appear in the flue gases.

According to Warner et al.,[505] at incineration temperatures of 170-300 C, the polyvinylchloride in refuse being incinerated decomposes, giving off hydrogen chloride. At temperatures above 300 C, ignition is well advanced; at 400-700 C, where the main burning occurs, the gaseous products are a mixture of water, carbon monoxide, carbon dioxide, and hydrogen chloride from any chlorine-containing compounds present (including inorganic chlorides, such as salt).

Warner et al.,[505] recognize the difficulties of attempting to correlate and compare data from different sources as to the classification of solid wastes, but indicate that it is clear that the composition of refuse has changed since 1939. In particular, ashes have largely disappeared and been replaced with combustible material, such as paper and plastics, whereas the amounts of other inorganic materials, such as glass and metals, have increased.

According to a survey made for the Department of Health, Education, and Welfare,[102] the packaging industry contributed 51.7 million tons to the total residential, commercial, and industrial waste load in the United States in 1966. The plastic content of that contribution was estimated to represent approximately 2% of the United States total "collectible refuse" load.

Warner et al.,[505a] indicate that the fraction of plastic in the solid waste load in 1980 is expected to be about 2.8%, up from 2% in 1970. They also indicate that Debell and Richardson, Inc., estimates indicate that in 1970 about 54% of the plastic solid waste was polyolefin, about 20% polystyrene, about 11% polyvinylchloride, and 15% all other, including cellulosics. For packaging wastes only, polyolefins are nearly 75%, polystyrene nearly 20%, and polyvinylchloride a little over 6% of the "big three" totals.

Huffman and Keller[222] indicate that the total amount of plastic found in the waste stream in 1970 has been estimated at 3.25 million tons, or about 2% of the municipal solid waste load, and that 70% of this waste plastic is polyethylene and polypropylene, 17% is polystyrene, and the remaining 13% is polyvinylchloride (or about 0.26% of the municipal refuse). Warner et al.[505a] conclude that the present polyvinylchloride content in collectible refuse is 0.20-0.25%, compared with 0.1-0.5% in the other countries of the world (except Japan, where it is 2-3%). According to a 1971 report of the National Industrial Pollution Control Council,[355a] polyvinylchloride makes up less than 0.15% of all collected household, commercial, and industrial waste.

In a recent investigation by Kaiser and Carotti[262] of the chlorine contents of refuse components, all organic fractions were found to contain some chlorine, probably largely as sodium chloride. Less than half the chlorine was present in chlorinated plastics.

It is possible to estimate the maximal hydrogen chloride emission potential from refuse incineration in the United States through use of the above and other cited data. Thus, assuming a polyvinylchloride content of 0.25% in collectible refuse and a chlorine content of 50% for the polyvinylchloride component, an estimated refuse chlorine content of 0.125% would be contributed by the chlorinated plastic component. If, in addition, less than half the chlorine present in the refuse is due to the chlorinated plastic contribution, a total refuse chlorine content of 0.25% may be calculated. Although only limited data are available on the direct determination of the chlorine content of refuse, Kaiser and Carotti[261] list a 0.50% chlorine content of a typical municipal refuse, and a Horner and Schifrin, Inc., report done under an EPA grant[226] lists a 0.13-0.32% chlorine content based on analysis of three samples of residential solid waste. If it is assumed that the average chlorine content of refuse is 0.25%, the maximal atmospheric emission potential for hydrogen chloride gas due to the incineration of refuse in 1970 was 75,000 tons.

Although the average chlorine content of municipal refuse appears to be 2-3 times the average chlorine content of coal, the quantity of coal burned in the United States each year is approximately 20 times as great as the amount of municipal refuse incinerated.

Increased emphasis on removal of particles from the gases emitted from incinerator stacks will promote the installation of the very efficient wet scrubbers for control of this pollution problem. Wet scrubbers also provide favorable conditions for removing such gases as sulfur dioxide and hydrogen chloride and organic acids out of the flue-gas stream. However, these gases tend to form active acids in water solution, and the scrubbers, ducting, fans, and stacks must be constructed of materials that can withstand acid corrosion.

It is only in the last few years that true wet-scrubbing systems, as differentiated from crude spray chambers or wet baffles, have been applied to municipal incinerators, and fewer than 10% of the incinerators have them.[505]

Transportation

Although emission of particulate matter, including chlorides, in automotive exhaust[218] and aerosols presumably formed by such emission[517] have been studied for some time, there appears to be little or no published information on the measurement of gaseous chlorine or hydrogen chloride in exhaust from any mode of transportation.[161, 446, 447, 492, 493] In fact, there is no evidence that such gaseous emission exists. Hydrogen chloride, if present, would probably exist as hydrochloric acid aerosol, because of the water in exhaust.

Although there are no data, one can calculate the maximal theoretical amount of gaseous chlorine or hydrogen chloride that could be emitted from mobile sources. In this discussion, the gaseous combustion product is assumed to be hydrogen chloride. The major source of this chlorine would be the ethylene dichloride scavenger used with lead antiknock compounds. Some other organically bound chlorine may be present in hydrocarbon fuels, but analysis of several naphthas showed chlorine concentrations of about 1-6 ppm,[33] a very low concentration when compared with about 300 ppm, which may be present in leaded gasoline as part of the antiknock additive. Lead antiknock compounds are not used in diesel and jet fuel, and those used in aviation gasoline do not contain a chlorine scavenger. Therefore, the only fuel to be considered as a significant source of chlorine is motor gasoline. The calculation can be made as follows.

Data from the U. S. Department of the Interior, Bureau of Mines, show 1971 domestic gasoline consumption at 92, 953 million gallons.[9] The aviation gasoline volume was 751 million gallons, leaving 92, 202 million gallons. An arithmetic average of data from more than 50 U. S. cities[153] indicates that premium-grade gasoline sales were 49. 3% of the total, or 45, 456 million gallons. The remaining 50. 7%, or 46, 746 million gallons, is assumed to have been regular grade, although it also includes subregular and super-regular or middle-premium fuels. The average of data from two Bureau of Mines motor gasoline surveys[422,423] showed that the average lead content was 2. 55 g of lead per gallon for premium grades and 2. 05 g/gal for regular grades. A small amount of gasoline is unleaded, although sales data are generally not made public. The unleaded premium gasoline sold in the eastern and southern states does not present a problem, because samples of this gasoline are included in the Bureau of Mines average for all premium grades. The subregular unleaded gasolines, however, are not included in the regular-grade average; therefore, the calculated total volume of regular-grade fuel, 46,746 million gallons, should be reduced by perhaps 0.5%, resulting in a leaded regular-grade volume of 46,512 million gallons. Using the average lead contents of regular and premium fuels and the volumes of each, the total amount of lead used in antiknock compounds in the U. S. in 1971 was 211,263,000 kg, or about 232,900 tons. (The Bureau of Mines reported that about 264,000 tons of lead was used for production of antiknock compounds,[494] but some of the product was exported.[459]

According to Ethyl Corporation,[136] the composition of tetraethyl lead (TEL) motor mix is as follows:

	wt %
lead alkyl	61.48
dye	0.0621
ethylene dibromide	17.86
ethylene dichloride	18.81
inhibitor and inerts	1.79

The chlorine:lead weight ratio in the mixture is 0.342:1. The total amount of lead used in antiknock compounds was calculated to be about 232,900 tons, so the amount of chlorine used would be about 79,650 tons.

The major particulate matter in automotive exhaust is reported to be lead II bromide chloride ($PbClBr$),[218,472] but other chlorine-containing solids have also been identified, such as the ammonium lead II bromide chloride complexes ($2NH_4Cl \cdot PbClBr$ and the alpha and beta forms of $NH_4Cl \cdot 2PbClBr$).[218] Average data from two vehicles operating both on a city driving cycle and at a constant 60 mph indicate the following product distribution (the calculated chlorine:lead weight ratio for each compound is also shown):

	wt %	Cl:Pb (wt)
$PbClBr$	48	0.171:1
$NH_4Cl \cdot 2PbClBr$	45	0.257:1
$2NH_4Cl \cdot PbClBr$	7	0.513:1

The composite chlorine:lead weight ratio in the particulate-product mixture is then calculated to be 0.234:1. If all the lead used in antiknock additives, about 232,900 tons, is converted during combustion to those three compounds, the amount of chlorine in the mixture would be 54,500 tons. The remaining chlorine, about 25,150 tons, would then conceivably be emitted as about 25,870 tons of hydrogen chloride. This is the maximal amount of hydrogen chloride that could be emitted from the combustion of motor gasoline in the United States. The quantity actually emitted is probably much less. It seems reasonable to assume that other chlorides may be formed, such as lead dichloride and ammonium chloride, as well as hydrocarbon chlorides, thereby reducing the amount of hydrogen chloride. It is also probable that a small amount of the hydrogen chloride ends up in the crankcase oil.

In comparison with the maximal calculated hydrogen chloride emission of 25,870 tons, Gerstle and Devitt estimated that gasoline combustion may have contributed only 4,500 tons of hydrogen chloride in 1969, or only about 0.5% of the total from all combustion processes.[161] These authors also indicate that gaseous chlorine does not result from combustion. In any case, hydrogen chloride emission from mobile sources will decrease in future years, as the lead content of gasolines is decreased.

Some indication of this reduction can be obtained from Figure 2-1, displayed[362] by William Ruckelshaus, former EPA Administrator. The figure demonstrates that mobile-source lead emission will decrease drastically, as the use of unleaded gasoline increases owing to catalytic emission control system requirements (top curve). If, in addition, EPA imposes phased reduction of the average lead content of all motor fuels, the overall lead emission reduction would be even faster (bottom curve).

Concurrent with the reduction in mobile-source lead emission is the obvious reduction in chlorine-compound emission. The EPA estimates that about 200,000 tons of lead will be emitted in 1973 from mobile sources. This is equivalent to a maximal hydrogen chloride emission of about 22,000 tons. The maximal hydrogen chloride emission from 1973 to 1985 would be reduced in proportion to the reduction in lead emission shown in Figure 2-1. For instance, with lead reduction only through the phasing in of lead-free gasoline, maximal hydrogen chloride emission will be less than about 10,000 tons/year by 1978 and less than about 5,000 tons/year by 1982. If, in addition, EPA imposes the phased reduction of the average lead content of all gasolines (as shown in the figure), maximal hydrogen chloride emission will be less than about 10,000 tons/year by 1976 and less than about 5,000 tons/year by 1978.

Automated-Mission Spacecraft

The NASA Office of Space Science Launch Vehicle and Propulsion Programs is responsible for the launch of approximately 20 automated spacecraft per year. These spacecraft contribute in a variety of ways to the control and betterment of the environment (e.g., meteorologic satellites). However, adverse environmental effects might result from these activities with respect to air quality, water quality, noise, and reentry of launch-vehicle debris. No chlorine emission to the atmosphere in association with rocket tests, launches, on-pad accidents, or in-flight abort situations has been observed or postulated.

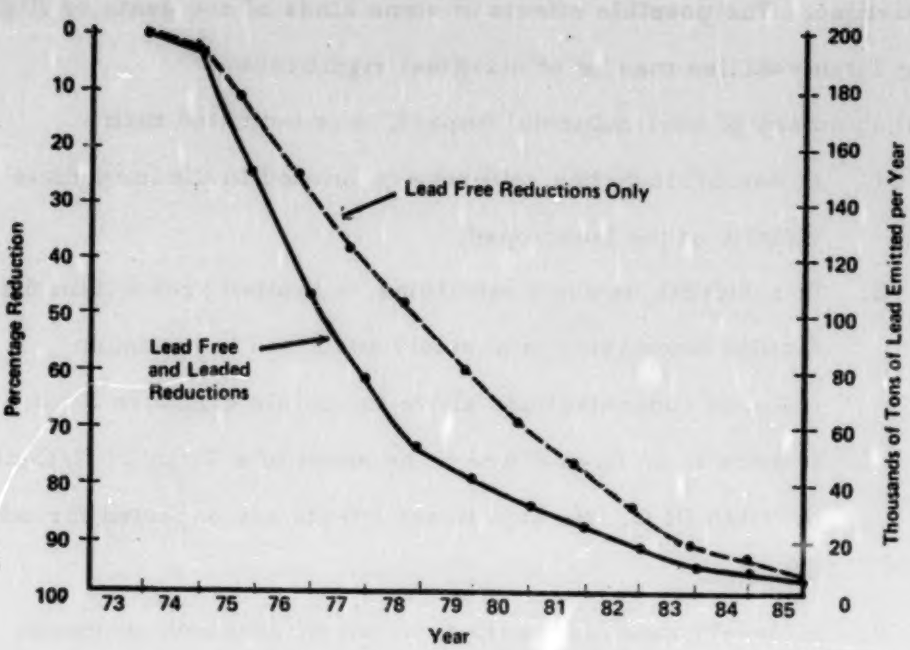

FIGURE 2-1. Projected reductions in lead emission resulting from EPA lead regulations.

A 1973 final environmental statement of NASA OSS launch vehicles and propulsion programs indicates that environmental pollution by these vehicles appear to be very low.[355] This conclusion is supported by Table 2-2 (from the final environmental statement), which compares various emission sources. No significant impact is expected from normal current and planned NASA spacecraft activities. The possible effects of some kinds of accidents or flight failures involving Titan vehicles may be of marginal significance.

In a summary of environmental impact, it is indicated that:

1. In normal launches, effects are limited to the immediate vicinity of the launch pad.
2. In accidents or abort situations, a limited area within the facility boundaries is possibly subjected to hydrogen chloride concentrations above the public exposure limit, if there is an on-pad fire or an abort of a Titan III E/Centaur or Titan III C. No significant effects are expected for other vehicles.
3. In development and testing, no significant environmental effect is produced. The Titan III E/Centaur (in development) and the Titan II C (operational) are NASA's largest vehicles in terms of quantity of propellant, total vehicle mass, length, diameter, and thrust at zero altitude. Table 2-3 summarizes the estimated maximal radius of ground-level effects for Titan III E/Centaur or Titan III C. Table 2-4 lists the reported and estimated human, plant, and animal exposure criteria used to estimate the environmental impact of propellant and combustion-product air pollutant emission that might arise from normal and emergency NASA OSS launch vehicle and propulsion program activities.

TABLE 2-2

Comparison of Emissions into the Lower Atmosphere *

	Emission, 10^6 kg/year				
	CO	NO_x	HCl	SO_2	Ash
NASA Launch Vehicles					
for automated missions[a]	0.414	0.00014	0.060		0.11[d]
Automobiles[b]	56,200	5,720	4.1[c]	--	--
Power Plants[b]	90	3,200	610[c]	13,400	4,400
Trash Incineration[b]	6,890	450	180[c]		--
Jet Aircraft[b]	270	90	--	--	--

---

[a] Based on first stage propellants, 1969-1971 average.

[b] For 1966. Source: "The Federal R&D Plan For Air-Pollution Control By Combustion-Process Modificaton", January , 1971, PB 198-066.

[c] Estimates from Gerstle and Devitt, "Chlorine and Hydrogen Chloride Emissions and Their Control", Paper No. 71-25, Air Pollution Control Association, 1971.

[d] Al_2O_3 from solid propellants.

*Reprinted from National Aeronautics and Space Administration[355]

TABLE 2-3

Summary of Estimated Maximum Radius of Ground Level Effects for Titan IIIE/Centaur or Titan IIIC *

Event	Maximum Radius at which Exposure Exceeds Criteria	Limiting Pollutant	Criteria Used **
Normal Launch	2.4km	HCl	4ppm
Cold Spill	6km	N_2O_4	2ppm
On-pad Catastrophe	Criteria Not Exceeded	HCl	7ppm
Low Level Destruct	Criteria Not Exceeded	HCl	7ppm
Engine Test	Criteria Not Exceeded	CO	30ppm

*Reprinted from National Aeronautics and Space Administration[355].

**For uncontrolled populations. Criteria for normal operations assumed for normal launch and engine test. Emergency criteria used for accidental exposures.

TABLE 2-4 - EXPOSURE CRITERIA FOR SOME COMBUSTION PRODUCTS AND PROPELLANTS

Substance	Controlled Populations(a)				Uncontrolled Populations(b)						Plants		Animals
	TLV,(c) ppm	Short-Term Emergency Limits(5), ppm			Exposure from Ordinary Operations, ppm			Emergency Exposure, ppm			Sensitive (i)	Resistant (i)	
		10 min.	30 min.	1 hr.	10 min.	30 min.	1 hr.	10 min.	30 min.	1 hr.			
HCl	5	30	20	10	4(d)	2(d)	2(d)	7(d)	3(d)	3(d)	5/2(14)	1000/1(14)	Human exposure criteria are normally based on experimental animal exposures using a number of species and considering the most sensitive species tested. Hence, human exposure criteria are probably applicable to most animals. Birds could be an exception as they are rarely used as test animals.
CO	50			200			30(e)		—	125(8)	500/-(49)(j)	100,000/-(50)(k)	
Al_2O_3 (mg/m^3)	10	50(9)	25(9)			—			—		—	—	
NO_2 (N_2O_4)	5	30	20	10	1(f)	1(f)	1(f)	5(f)	3(f)	2(f)	2.5/2(14)	1000/1(14)	
Hydrazine	1	30	20	10	1(g)				—		<25/4(51)	-25/4(51)	
UDMH	0.5	100	50	30	0.5(g)				—		<31/4(51)	-31/4(51)	
$AlCl_3$ (mg/m^3)	10(h)		—			—			—		—	—	

(a) Controlled populations consist of persons with known medical histories, subject to periodic health checks, and generally under the control of the responsible agency. Such persons are normally employees with jobs that will potentially result in exposure to known contaminants.

(b) Uncontrolled populations consist of persons with unknown medical histories, not subject to periodic health checks, and not generally controlled by the responsible agency. The general public is included in this classification.

(c) No short duration exposure criteria for controlled populations appear applicable for ordinary launch operations. Threshold Limit Values (TLV) are time-weighted concentrations for 7 or 8 hour work days and a 40-hour work week, except that the values for HCl and NO_2 are also considered ceiling values not to be exceeded.(4) TLV's are thought to be conservative for short duration exposures of controlled populations for relatively infrequent normal operations.

(d) While there are no criteria for short-term exposure of uncontrolled populations to HCL which have official standing, the values quoted here have been proposed by a responsible organization after careful study of the problem (See Reference 6)

(e) Based on 1.5% Carboxyhemoglobin in 1 hour exposure. See Reference 7.

(f) There are no officially accepted criteria for short-term exposure of uncontrolled populations to nitrogen oxides. The criteria given here have been proposed by a responsible organization after careful study. (See Reference 10).

(g) Arbitrarily set equal to the 8 hour industrial TLV: i.e., 1/48 of the acceptable industrial dose.

(h) Based on hydrolysis to HCl. In subsequent discussion, $AlCl_3$ is considered only in terms of its contribution to overall HCl levels.

(i) Concentration in ppm/exposure time in hours.

(j) Epinastic response in tomatoes. Toxic response (leaf abscission) generally observed at ~1% CO for 1 to several days.

(k) No observable effect on Nephrolepis in an exposure of 1 to several days.

(Reprinted from National Aeronautics and Space Administration;[355] reference numbers pertain to references in original publication.)

The final environmental statement concludes that hydrogen chloride emission from the Titan vehicles represents the only environmental hazard of significance. It concludes that this hazard is modest; even under unfavorable meteorologic conditions, it is assumed to be confined to controlled areas.

The final environmental statement assesses the environmental effects of operations involving the current and near-future launch vehicles that will be used up to about 1980. The Space Shuttle, which is intended to replace most of the current family of launch vehicles and is expected to be operational by about 1980, will use a main engine propellant consisting of a mixture of liquid hydrogen and oxygen; the propellant will produce only water vapor and free hydrogen from the combustion process.[354]

EMISSION CONTROL

Chlorine

In the chlor-alkali industry, emission of chlorine originating from blow gases, tank-car blowdowns, air-blowing of mercury-cell brine, and air-padding of liquid-chlorine storage tanks can be prevented or controlled by using the chlorine so produced for chemical requirements within the plant; neutralizing the chlorine in alkaline scrubbing units to form disposable, nonvolatile substances, such as calcium and sodium hypochlorites; or scrubbing the chlorine from the gas streams with a solvent like water, alkaline brine, or carbon tetrachloride and recovering the chlorine.

The principal emission from chlorine manufacture is the chlorine present in the noncondensable gases that are separated from liquid chlorine during liquefaction. If liquid chlorine is not produced (as in a paper mill plant), the plant will have no blow gas and therefore no chlorine emission from this source. Where liquid chlorine is produced, emission varies according to the waste treatment system and the chlorine content of the blow gas. Table 2-5 shows the concentrations and amounts of chlorine that may be emitted with or without control system.

TABLE 2-5

Chlorine Emission from Liquefaction Blow Gases in Diaphragm- and Mercury-Cell Plants[a]

Type of Control	Chlorine Concentration in Exhaust, vol %	Chlorine Emission Factor, lb/100 tons of chlorine liquefied
None	20-50	2,000-16,000
Water absorber	0.1-4.5	25-1,090
Caustic or lime scrubber	0.0001	1

It is common practice to operate at condensing pressures and temperatures that represent an economic optimum. If chlorine in the blow gas will not be used and chlorine must be neutralized, it is economical to condense at higher pressures or lower temperatures, or both, to reduce the chlorine in the blow gas. If useful byproducts can be made or the chlorine in the blow gas is recycled or recovered in some other manner, it is usually more economical to allow the chlorine concentration in the blow gas to increase in lieu of operating at relatively high pressures or low temperatures, or both. The quantities of chlorine in blow gas are increased by operating above cell rated capacity when the chlorine condensing facilities are adequate only at rated capacity and by having air in the system on startup of a new cell circuit or after a shutdown, which seriously reduces the liquefaction efficiency.

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[a] Derived from Cooperative Study Project.... 87

Table 2-6 summarizes present practices for the treatment of chlorine in blow gas as reported in 24 questionnaire responses.

TABLE 2-6

Processing of Blow-Gas Chlorine[a]

Process Used	No. Plants
Sent to alkaline scrubbing equipment	7
Sent to absorptive scrubbing equipment	4
Vented to atmosphere	0
Sent to in-plant processes	11
Not indicated	2
Total	24

Tables 2-7 and 2-8 give emission and operating data from chlor-alkali establishments using blow-gas treatment. Table 2-9 gives data on handling chlorine from shipping-container vents during loading, as reported in 19 questionnaire responses. In all cases except two, chlorine removed during tank-car loading was transferred to other plant uses, returned to the process, or treated in a scrubber. In the two exceptions, collection was not complete, and chlorine was vented at 10 and 140 lb/day.

In-Plant Utilization of Chlorine-Containing Blow Gas or Waste Gas in the Chlor-Alkali Industry. Waste chlorine has been used to manufacture chlorobenzene,[150] hydrochloric acid, sulfur monochloride,[460] and bleach.[273] It has also been used to chlorinate river water to prevent algae buildup in cooling towers and to treat waste water before discharge.[87]

---

[a] Derived from Cooperative Study Project. . . [87]

TABLE 2-7

Emission and Operating Data from Chlor-Alkali Establishments using Blow-Gas Treatment[a]

	Plant number						
	28	29	30				31
Chlorine production, tons/day	490	140	180[b]	170[c]	149[c]	119[c]	316
Liquid chlorine capacity, tons/day	370	140	180[b]	170[c]	149[c]	119[c]	316
Cell type[d]	M and D	M	D				M
Description of control equipment	Two milk-of-lime falling film towers	Two caustic-packed towers in parallel	Packed-tower water absorbed under pressure				Two milk-of-lime cascade baffle towers in parallel
Tower diameter, in. OD	56	52[e]	42				60
Height of packing, ft	30.5[f]	6.83	29				12[f]
Type of packing	None; 4-in. standard pipe launderer	2-in. Intalox saddles and ceramic tiles	Alternately stacked 1- and 1-1/2 in. Intalox saddles				None; 3-ft overlapping baffles
Materials of tower construction	Concrete sections	Titanium-lined steel	Rubber-lined steel				Hetron, glass-matte reinforced
Sources of inlet chlorine	Blow gas, process blowdown, tank car venting	Blow gas, brine blowing, process blowdown, tank car venting	Blow gas only				Blow gas,[g] cell end boxes, tank car vents
Scrubbing liquor and strength at test, % by wt	$Ca(OH)_3$ 17	NaOH 4 and 17	H_2O				$Ca(OH)_2$ 3.2
Liquor circulation rate, gal/min	550	75	115	112	112	112	200
Liquor temperature, °F	N.M.[h]	N.M.	52	75	75	75	109
Scrubber pressure drop, in. H_2O	2.5	2	3	4	4	3.5	2
Scrubber							
Inlet gas rate, scfm at 32° F, 1 atm wet	N.M.	N.M.	191	184	163	139	N.M.
Outlet gas rate, scfm at 32° F, 1 atm wet	456	4,140[i]	171[j]	151[j]	127[j]	106[j]	1,120[i]
Inlet chlorine concentration, vol %, wet	19.7	0.325	14.4	14.1	13.9	13.1	1.41
Outlet chlorine concentration, vol %, wet	0.0009	N.D.[k]	4.46[l]	1.55	0.44	0.1	0.0008
Inlet carbon dioxide concn., vol %, wet	N.M.	N.M.	18.0	22.4	22.4	22.3	N.D.
Outlet carbon dioxide concn., vol %, wet	N.M.	N.M.	19.6	21.6	18.6	15.2[m]	N.D.
Chlorine mass efficiency, %	99.9	>99.9	72.5[l]	91.0	97.4	99.4	>99.9
Chlorine emitted, lb/day	1.16	None	2,130	659	158	29.6	0.284
Chlorine emission factor, lb chlorine/100 tons chlorine liquefied	0.314	None	1.090	388	106	24.9	0.095
Stack plume opacity, %	80	40	N.O.[o]	N.O.	N.O.	N.O.	–[n]

[a] Based on sampling by the Public Health Service.

[b] Actual liquid production at time of test was 195 tons/day. Production changed to 180 tons/day to agree with total chlorine in blow gas/100 tons chlorine liquefied for tests 2, 3, and 4 performed at a later date.

[c] Liquid production based upon absorber chlorine load.

[d] D = diaphragm; M = mercury.

[e] Inside diameter.

[f] Height of towers, no packing employed.

[g] After scrubbing in alkaline brine.

[h] Not measured.

[i] Combined exhaust rate from both stacks.

[j] Calculated by material balance.

[k] Not detected.

[l] Foaming present in scrubber.

[m] Determined by extrapolation.

[n] Exhaust sent to powerhouse stack.

[o] No observation.

[a] (Reprinted from Cooperative Study Project....)

TABLE 2-8

Questionnaire Emission Data from Chlor-Alkali Plants with Blow-Gas Treatment Equipment

	Plant number										
	1	4	7	9	10	12	13	14	18	22	25[a]
Type of cell	D[b]	D	D	D	M	M	M	M	M	M	D
Rated capacity, tons/day	240	50[c]	65	50	230	260	130	112	262	180[c]	458[d]
Scrubbing liquor	5% NaOH	5% NaOH	H_2O	$Ca(OH)_2$[e]	$Ca(OH)_2$	$Ca(OH)_2$	Na(OH)	Waste alkali[f]	CCl_4	–	H_2O
Liquor flow, gal/min	25	10	80	N.A.[g]	2	600	73	50	17	–	550
Inlet liquor conditions											
Nominal Cl Concn., g/liter	60	1	0	N.A.	0	10	0	0	0.01[h]	–	0
Temperature, °C	21	20	20	N.A.	30	30	28	30	-18	–	32.2
Outlet liquor conditions											
Nominal Cl concn., g/liter	120	2	?	N.A.	150	20	33	?	9.4[h]	–	1.23
Temperature, °C	21	22	20	N.A.	30	32	40	35	10	–	32.2
Tower diameter, in.	30	10	24	N.A.	72	72	72	72	42[i] 29[j]	38	48
Height of packing, ft	17	20	30	N.A.	32	32	20	40	50[i] 50[j]	20	20
Type of packing	2-in. Raschig rings	1-in. Raschig rings	1.5-in. Intalox saddles	N.A.	Spray tower	Raschig rings	Chemical stoneware rings	8- x 12-in. clay tile	Plates[j] 1-in. Raschig[i]	3-in. ceramic partition rings	2-in. ceramic Berl saddles
Materials of construction	Rubber-lined steel	Rubber-lined steel	Rubber-lined steel	N.A.	Concrete	Concrete	Concrete	Concrete	Steel	Rubber-lined steel	Rubber-lined steel
Inlet gas temp., °C	4	-60	25	35	20	40	3	35 to 40	100	-10	-38
pressure, psig	2	0.1	35	35	0.5	0.14	15	35	95	5	35
chlorine, vol. %	2	0.1	26	7	9	1	15	7	30	5.2	11
Outlet gas temp., °C	21	-10	20	–	25	32	40	30 to 35	30	20	32.2
pressure, psig	0	0	34.66	0	0	0	0	0	40	0	35.0
chlorine, vol. %	0	0	3	0	0	0	0	N.D.[k]	0	0.5	0.3[a]
Outlet gas flow, scfm	1,078	8	14.5	180	390	600	120	370	–	510	202
Efficiency of scrubber, %	100	>99	1	>99	100	100	100	>99	100	90	97
Total chlorine emitted, tons/day	nil	<0.1	0	N.A.	N.D.	N.D.	N.D.	N.D.	nil	0.4	0.084
Lb chlorine emitted solidus 100 tons of liquid chlorine	–	<400	–	–	–	–	–	–	–	<400	54

[a] Design data.

[b] D = diaphragm; M = mercury.

[c] All output is liquid Cl_2.

[d] Liquid Cl_2 product = 308 tons/day.

[e] Reported use of vats containing $Ca(OH)_2$ slurry.

[f] NaOH, $NaHCO_3$, Na_2CO_3.

[g] Not applicable.

[h] Mole %.

[i] Stripper.

[j] Absorber.

[k] Not detectable by odor.

[l] Water absorber vented to caustic scrubber; chlorine emissions reported as zero.

(Reprinted from Cooperative Study Project....)

TABLE 2-9

Questionnaire Data on Handling of Chlorine from Shipping-Container Vents During Loading

	Plant number																		
	1	2	3	4	6	7	8	9	10	11	12	13	14	15	19	20	21	22	25
Rated capacity, tons/day	240	180	150	50	70	65	180	50	230	79	260	130	112	254	222	138	190	180	458
Liquid capacity, tons/day Cl_2	240	a	a	50	a	69	a	a	230	a	250	100	112	a	a	a	a	100	308
Quantities of Cl_2, from tank car loading, tons/day	2	0.1	0.1	0.2	<0.1	<1.0	2.0	0.25 to 0.50	0.2	1 to 2	1	3.0	2.0	1.0	1.0	1.0	243	0.3	5.6
Frequency of tank car loading, no./day	3	2[b]	1	1	c	a	a	1	d	e	1	e	f	2	1	d	g	25	g
Tons of chlorine evolved/55-ton tank car loading	0.67	0.35	0.1	0.2	–	–	–	0.25 to 0.50	–	–	1.0	–	–	0.5	1.0	–	–	0.01	–
Tons of chlorine evolved/100 tons of chlorine liquefied	0.84	0.055	0.067	0.4	<0.14	<1.45	1.1	0.5 to 1.0	0.087	1.3 to 2.5	0.40	3.0	1.8	0.39	0.45	0.72	1.28	0.167	1.22
Treatment of tank car waste chlorine:																			
Scrubber	x	–	x	x	x	–	–	x	x	–	x	x	x	–	x	–	–	x	x
In-plant	–	x	–	–	–	x	x	x	–	x	–	–	–	x	x	x	x	–	–
Vent	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	h	i	–	–

[a] Unknown.
[b] Per week.
[c] Rare.
[d] Intermittent.
[e] 8-hr day.
[f] 6-hr day.
[g] Daily.
[h] 0.5 % vented = 10 lb/day.
[i] 140 lb/day vented.

87

(Reprinted from Cooperative Study Project. . . .)

__Absorption of Chlorine without Recovery__. Alkaline scrubbers that use caustic or lime to react with waste chlorine to form sodium and calcium chloride and hypochlorite are suited for treating dilute tail gases (less than 1% chlorine). When chlorine concentrations are higher several percent-- other control methods that permit recovery of pure chlorine are more attractive economically. Absorption efficiencies of nearly 100% are attainable in alkaline scrubbers at modest equipment cost. Waste chlorine in the blow gas from the liquefaction system and that originating from the air-blowing of depleted brine and other sources are generally combined and sent to a packed tower using caustic liquor or a spray tower using a lime slurry. Recent developments in improved scrubber design include the use of high-density polyethylene or polypropylene packing shapes and the increase use of fiber-reinforced plastics (FRP) to replace stainless steel, rubber- and polyvinylchloride-lined steel, and other metallic alloys for scrubber bodies.[424]

Both reactions that can be used to remove chlorine in alkaline scrubbers,

$$2NaOH + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$$

and

$$2Ca(OH)_2 + 2Cl_2 \longrightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O,$$

are exothermic, proceed rapidly to completion, and are irreversible over a wide range of concentrations, if high temperature and low pH are avoided.[154]

Seven of the 24 plants that responded to questionnaires in the cooperative study cited previously[87] use alkaline scrubbers to control blow-gas emission, and the absorption efficiencies exceeded 99% in all of them (Table 2-8). Source tests were performed on two lime scrubbers and one caustic scrubber. Absorption efficiencies of 99% or higher and exit chlorine concentrations of less than 10 ppm in the vents were found in all three cases.

Alkaline scrubbing systems are used extensively in the chemical process industry, to remove chlorine from chlorination process tail gases being emitted to the atmosphere. Alkaline scrubbing normally takes place after organic or inorganic chemical removal, such as condensation, solvent scrubbing, or water scrubbing for hydrogen chloride absorption.

The formation of hypochlorites in waste chlorine gas neutralization by alkaline media creates a pollution control problem within the plant confines and with respect to external receiving waters. If the hypochlorite is not decomposed, chlorine gas will be released on contact with acid streams. To eliminate the hypochlorite disposal problem, the hypochlorite is decomposed in the scrubber with heat and a low concentration of metallic ion catalyst (Hooker Chemical Corporation, private communication). The hypochlorite ion is decomposed to innocuous chloride ion and oxygen:

$$\mathrm{OCl^-} \xrightarrow[\text{catalyst}]{\Delta} \mathrm{Cl^-} + \frac{1}{2}\,\mathrm{O}^{2}$$

Recovery of Chlorine by Absorption and Stripping. In contrast with scrubbing systems that involve neutralization and disposal of chlorine, various absorption techniques can be used to recover waste chlorine. This is especially useful where high chlorine concentrations (greater than 10%) favor economical recovery. Such systems contain an absorber to remove chlorine from the gas stream and a stripper to recover the absorbed chlorine from the rich absorbing liquor. Collection efficiencies are generally better than 90%.[87]

Blow-gas columns using water for absorption are particularly useful in some diaphragm-cell chlorine plants. A cooler-stripper is integrated into the main cell chlorine purification system. Cold water is passed countercurrently to the chlorine-containing gas stream in an absorption tower filled with ceramic packing. Overhead gases, too low in chlorine for its economical recovery, can be sent to alkaline scrubbers or discharged to the atmosphere. Bottoms from the tower, rich in dissolved chlorine, are sent to a desorption tower consisting of a direct-contact cooler and a steam-stripping section. Hot chlorine-cell gas is used to strip the chlorine partially from the cold water while the cell gas is simultaneously cooled. The remaining chlorine is removed by direct contact with live steam. One such process is described in detail in a patent.[224]

Two diaphragm-cell chlorine plants indicated use of water absorbers in response to a questionnaire.[87] One of these, having an exit chlorine concentration of 3%, directs vent gases to a caustic scrubber that virtually eliminates chlorine emission to the atmosphere. The other uses an absorber designed to give an absorption efficiency of 97%, corresponding to an inlet-gas chlorine concentration of 11% and an exit-gas chlorine concentration of 0.3%. If vent gases are considered to contain chlorine in excess of allowable limits, absorption efficiencies as high as 99.4% can be obtained at a somewhat higher cost--the cost of steam used in stripping. As an alternative, a secondary water scrubber can be used, with the water effluent sent to disposal. In any event, it is good practice to provide an alkaline scrubber for emergency use, in case the chlorine in the vent gases becomes excessive.

Oldershaw _et_ _al_.[366] have described a system for the thermal stripping and recovery of chlorine from 32% hydrochloric acid produced in an absorber handling a feed-gas stream containing 75 mole % hydrogen chloride, 15 mole % chlorine, and 10 mole % inert substances.

Another type of blow-gas absorber uses carbon tetrachloride as the solvent to recover chlorine from gas streams.[82] Carbon tetrachloride contacts the waste chlorine in a packed tower and releases it in a steam-heated recovery tower consisting of a stripping section and a rectifying section. One questionnaire response[87] indicated that chlorine recovery in the absorber is nearly 100%. Stern[200] indicates that the recovery of chlorine is much more nearly complete when carbon tetrachloride, as opposed to water, is used as the absorbent.

An unpatented process[87] uses sulfur monochloride to recover waste chlorine through formation of sulfur dichloride in an absorber. Chlorine can be distilled from the dichloride and recovered, or the mixture of sulfur monochloride and dichloride can be marketed.

Patented systems include those using alkaline brine,[82] stannic chloride,[231] hexachlorobutadiene,[392] and ethylene dichloride.[264] The cited cooperative study[87] concludes that the alkaline brine system is used in mercury-cell plants to some extent, but that the other three systems have no commercial significance.

Adsorption Systems. A patented recovery system uses silica gel to adsorb chlorine from waste streams.[525] In a regeneration cycle, the adsorption zone containing silica gel with chlorine adsorbed thereon is subjected to reduced pressure, thereby desorbing chlorine and permitting its recovery. Thereafter, at least a portion of the previously recovered chlorine-free gas stream from the adsorption cycle is passed through the desorbed silica gel to strip the final traces of adsorbed chlorine. The recovery system is claimed to provide chlorine recovery efficiencies of 90-98% from noncondensable gases originally containing chlorine in concentrations below about 15%. Chlorine can also be removed from very dilute gas streams with activated carbon. The carbon can be reactivated by hydrogen gas at nominal pressure and temperature, forming hydrochloric acid, which can be readily absorbed in water.

Hydrogen Chloride

It has been indicated that the byproduct process accounted for 90% of the U.S. hydrochloric acid (100% basis) production in 1972. The hydrogen chloride is produced as a result of substitution chlorinations of organic compounds and the dehydrochlorination of saturated chlorinated compounds.

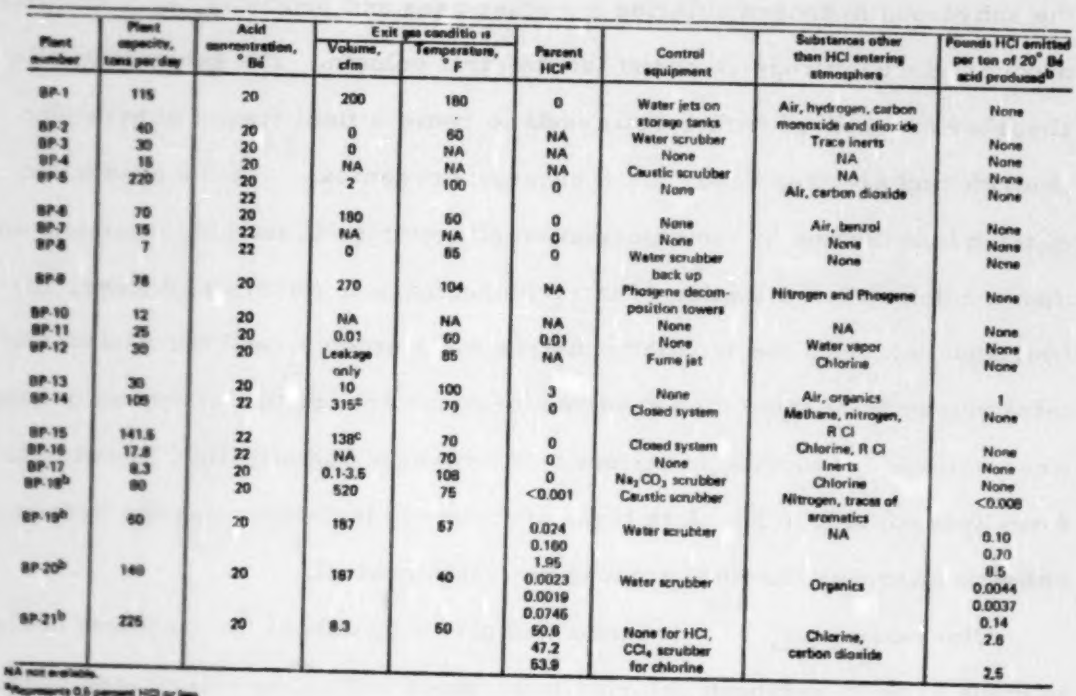
The use of anhydrous hydrogen chloride in hydrochlorination and oxychlorination reactions has dominated the use of hydrochloric acid (100% basis) in the production of organic chemicals in recent years. In processes using hydrochlorination (except hydrochlorination of alcohols) or oxychlorination, hydrogen chloride leaving the primary reactor is not absorbed in water, but is passed through an indirect-contact condenser for removal of condensable organics before the hydrogen chloride and noncondensable organics are recycled to the process. Hydrogen chloride is emitted only in the purge that removes inert materials from the recycled-gas stream.

Tail-gas concentrations of contaminants emitted from a typical byproduct plant are often reduced by scrubbing in a packed tower behind the final process tower. Venturi scrubbers are also used occasionally. If hydrogen chloride is the only component to be removed, water is universally used as the scrubbing agent, as shown in Table 2-10. Water scrubbers can reduce hydrogen chloride concentration to less than 0.1 lb/ton of acid produced. Alkaline scrubbing is sometimes used, if the gases contain substances like chlorine or phosgene, which are not readily absorbed in water.

Removal of organic materials from exhaust gases poses a separate design problem for each specific compound. In the chlorination of benzene, the hydrogen chloride from the reaction is scrubbed with recycled benzene for hydrocarbon removal and then absorbed in water forming 20 Bé hydrochloric acid (31.5% hydrogen chloride). A tail-gas absorber is also used, and the major air pollutant is benzene.[2] In the chlorination of methane to form carbon tetrachloride, the reactor effluent containing organic chlorides, hydrogen chloride, excess methane, and traces of chlorine is cooled and fed to the hydrogen chloride

TABLE 2-10

Emissions from By-Product Hydrochloric Acid Manufacturing Plants



Plant number	Plant capacity, tons per day	Acid concentration, ° Bé	Exit gas conditions		Percent HCl[a]	Control equipment	Substances other than HCl entering atmosphere	Pounds HCl emitted per ton of 20° Bé acid produced[b]
			Volume, cfm	Temperature, ° F				
BP-1	115	20	200	180	0	Water jets on storage tanks	Air, hydrogen, carbon monoxide and dioxide	None
BP-2	40	20	0	60	NA	Water scrubber	Trace inerts	None
BP-3	30	20	0	NA	NA	None	NA	None
BP-4	15	20	NA	NA	NA	Caustic scrubber	NA	None
BP-5	220	20 22	2	100	0	None	Air, carbon dioxide	None
BP-6	70	20	180	60	0	None	Air, benzol	None
BP-7	15	22	NA	NA	0	None	None	None
BP-8	7	22	0	65	0	Water scrubber back up	None	None
BP-9	78	20	270	104	NA	Phosgene decomposition towers	Nitrogen and Phosgene	None
BP-10	12	20	NA	NA	NA	None	NA	None
BP-11	25	20	0.01	60	0.01	None	Water vapor	None
BP-12	30	20	Leakage only	85	NA	Fume jet	Chlorine	None
BP-13	30	20	10	100	3	None	Air, organics	1
BP-14	105	22	315[c]	70	0	Closed system	Methane, nitrogen, R Cl	None
BP-15	141.5	22	138[c]	70	0	Closed system	Chlorine, R Cl	None
BP-16	17.8	22	NA	70	0	None	Inerts	None
BP-17	8.3	20	0.1-3.5	108	0	Na_2CO_3 scrubber	Chlorine	None
BP-18[b]	90	20	520	75	<0.001	Caustic scrubber	Nitrogen, traces of aromatics	<0.008
BP-19[b]	60	20	187	57	0.024 0.160 1.95	Water scrubber	NA	0.10 0.70 8.5
BP-20[b]	140	20	187	40	0.0023 0.0019 0.0746	Water scrubber	Organics	0.0044 0.0037 0.14
BP-21[b]	225	20	8.3	60	50.8 47.2 63.9	None for HCl, CCl_4 scrubber for chlorine	Chlorine, carbon dioxide	2.8 2.5

NA not available.

[a] Represents 0.5 percent HCl or less.

[b] Tested by PHS sampling team.

[c] Recycled—closed system.

(Reprinted from Cooperative Study Project. . . . 88) recovery system. The first column in this system is an absorber designed for efficient hydrogen chloride removal. The bulk of the absorbing liquor is the azeotrope in the hydrogen chloride-water system (about 20.24 wt % hydrogen chloride). The rich acid is thus above the azeotrope and allows stripping of anhydrous hydrogen chloride. The second column distills off the anhydrous hydrogen chloride for other uses and produces, as a bottoms product, the azeotrope required for the first column. The gases from the absorber are washed with caustic soda to remove final traces of hydrogen chloride and are then ready for recovery of organics.[2] In the production of trichloroethylene by the chlorination of acetylene to tetrachloroethane and then the dehydrochlorination of tetrachloroethane to trichloroethylene, the hydrogen chloride, the trichloroethylene main product, and the unconverted tetrachloroethane from the dehydrochlorinator are fed to a stripping column, where hydrogen chloride is stripped-off overhead and absorbed in water to form hydrochloric acid. A tail-gas absorber is installed after the hydrogen chloride absorber for final process emission control.[2]

Oldershaw _et_ _al_.[366] describe and give a flowsheet for a system designed to make 32 wt % hydrogen chloride from gases containing chlorinated hydrocarbons.

A study prepared for the Office of Air Programs of the EPA[2] contained the following general conclusions: Chlorination processes are usually designed to give high-efficiency containment of potentially hazardous emission of chlorine, hydrogen chloride, and chlorinated hydrocarbons within the process. They do not always have control equipment installed exclusively for the purpose of preventing emission, but typically they have gas-cleaning devices to collect unreacted gases and vapors, so that they can be recycled to the process. The cost and the obnoxious character of the materials provide incentives for high-efficiency (over 95%) cleaning of the exit gases. The collection methods are condensation, adsorption, and absorption. Condensers and solid adsorbents are generally used to collect materials for recycling to the process. The data available on adsorption are sparse, but metal oxides, molecular sieves, silica gel, activated carbon, and alumina have been used. The adsorbent is used to collect and concentrate dilute components in exit gases. Absorption systems are most commonly used for final gas-cleaning. Scrubbing liquids include water, caustic solutions, lime and limestone slurries, carbon tetrachloride, sulfur monochloride, benzene, and toluene. Where high-efficiency scrubbing is practiced with organics, absorbent losses will be the main atmospheric pollutant--e.g., where toluene or benzene is used to clean emission from equipment handling phosgene. Generally, because of the cost, such systems are used only for very hazardous materials.

Byproduct hydrogen chloride plants are adjuncts to other processes; therefore, they may be affected by upsets that occur in the process in which the hydrogen chloride is evolved. Good controls and secondary scrubbing systems can reduce the possibility of increasing emission resulting from such upsets.[88]

The design, operation, and maintenance of direct hydrogen chloride synthesis plants results in no significant emission of hydrogen chloride. During startup and shutdown, it is possible for chlorine and hydrogen chloride to be released into the air. Normally, an inert purge system is a part of the control system, and any chlorine, hydrogen, or hydrogen chloride present in the system is purged through the absorber-cooler and tails tower before a shutdown.[88] Other control and safety devices include automatic shutoff valves and seals on inlet gas lines, flame sensors, and ignition devices on the outlet duct to prevent the delivery of an explosive mixture of gases, instead of hydrogen chloride.

There are three basic methods of controlling atmospheric emission from Mannheim furnaces: proper operation, an efficient emission collecting system, and effective maintenance. Proper operation assumes good design and results in maximal product recovery, thus reducing the possibility of hydrogen chloride emission. An adiabatic wet-scrubbing tower that uses hydrochloric acid has had good results in scrubbing and cooling furnace gas. To reduce atmospheric emission, a scrubber system can be installed on the tails-tower exhaust. Scrubbers used for this purpose include venturi scrubbers and packed water-scrubbing towers.[88]

The most widely used hydrogen chloride absorption unit is the falling-film system. It consists of a falling-film cooler-absorber and a small packed tails tower.[196, 263] The gases and the absorbent, which is usually weak acid, enter at the top of the absorber, and the hydrogen chloride is absorbed in the liquid wetting the inside of the tubes. The absorption is limited by the number of tubes, which determines the amount of wetted area available for absorption and cooling. After passing through the falling-film absorber, the gases pass through a tails tower, where the remaining portion of the hydrogen chloride is reduced to less than 0.5% of the exit gas. Fresh water, used as the absorbent, is fed to the tails tower, and a weak acid feed to the top of the falling-film unit is the product.[88] A falling-film absorption system is shown in Figure 2-2.

The falling-film absorber's greatest virtue is its ability to produce strong acid (37-40%) without detectable vent loss. On the basis of equipment cost and technical factors--including desirable liquid loadings, feed-gas hydrogen chloride concentration, overall heat-transfer coefficients, and desirable gas velocities in the packed tail-gas scrubber--good engineering design indicates that the tail-gas scrubber should handle about one-third of the hydrogen chloride gas fed to

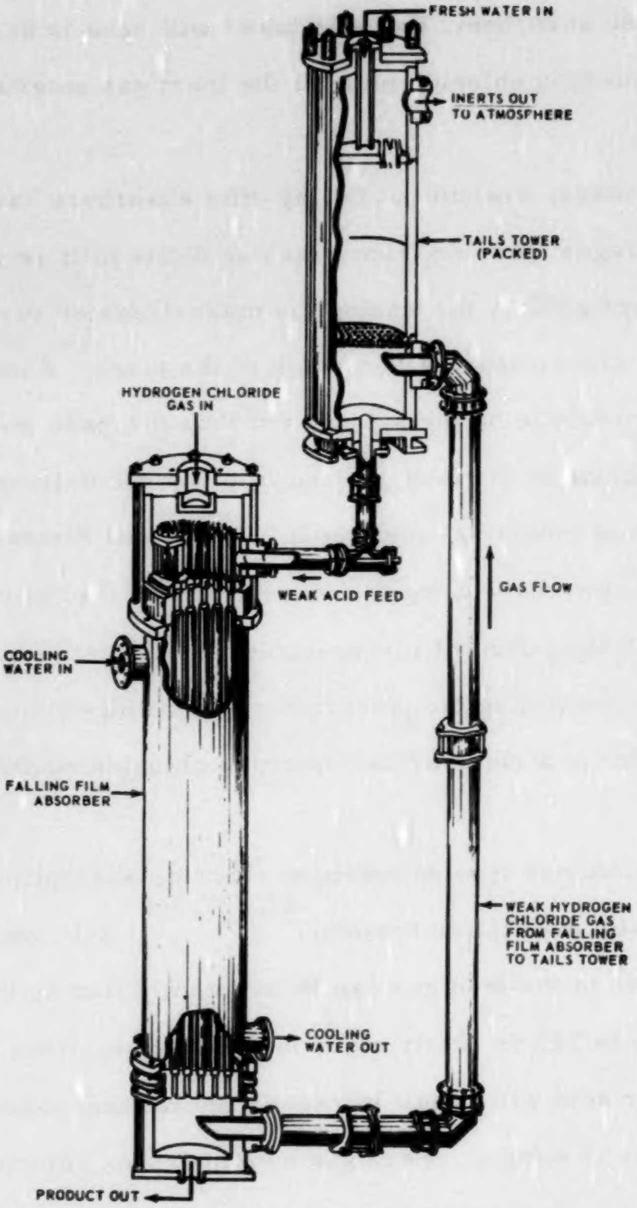

FRESH WATER IN
INERTS OUT TO ATMOSPHERE
TAILS TOWER (PACKED)
HYDROGEN CHLORIDE GAS IN
WEAK ACID FEED
GAS FLOW
COOLING WATER IN
FALLING FILM ABSORBER
WEAK HYDROGEN CHLORIDE GAS FROM FALLING FILM ABSORBER TO TAILS TOWER
COOLING WATER OUT
PRODUCT OUT

FIGURE 2-2. Falling-film absorber with external piping and tails tower.[88]

the cooler-absorber plus all the inert substances if water is the absorbent. If 20% acid is the absorbent, the tails tower will have to scrub only one-fourth of the hydrogen chloride plus all the inert gas entering the cooler-absorber.[276]

In recent years, systems of falling-film absorbers have been used for recovering hydrogen chloride from gases as dilute in it as about 5-10%. This has been accomplished by increasing the mass-transfer surface, adding one or two absorbers, and increasing the length of the tubes. Another method is to raise the total pressure on the system and thus increase the partial pressure of hydrogen chloride in the feed gas and improve the driving force.[276]

For design of industrial equipment, Gaylord and Miranda[156] have presented equations for correlating the mass-transfer coefficient for hydrogen chloride gas in falling-film absorber-coolers. Earlier work also covered correlations for predicting the performance of falling-film absorbers,[89, 109] and mass transfer in a commerical hydrogen chloride recovery unit has recently been studied.[37]

The other common type of hydrogen chloride absorption system is the so-called adiabatic absorption system.[87, 232, 366] Any concentration of hydrogen chloride in the feed gas can be accommodated by this equipment. Acid strength up to 34% is easily made in adiabatic systems. Attempts to produce stronger acid will result in rapidly decreasing absorption efficiency.

The process is simple. Feed gas with hydrogen chloride is introduced to the bottom of a packed contact tower, and the gas is countercurrently contacted by the absorbing medium, usually water. Weak acid may be used instead of or with water. If weak acid is the sole absorbent, the efficiency will range from 95% to more than 99%, depending on the weak acid concentration and the later hydrogen chloride vapor pressure. If pure water is the absorbing fluid, concentrated product acid can be made, with almost 100% recovery of hydrogen chloride.[232]

Because "adiabatic" absorption (the process is actually operated at constant temperature, rather than at constant enthalpy) is a hot process, pure hydrochloric acid can often be produced from contaminated feed gases. Byproduct hydrogen chloride from chlorination operations contains small quantities of chlorinated hydrocarbons. If these compounds have relatively low boiling points, they will not condense in the acid, and a high-purity product is made. However, compounds of high boiling point will condense and contaminate the product.

Hydrogen chloride emission from the falling-film and the adiabatic absorbers may be effectively controlled by installing any of several types of scrubbers after the tails tower (in the case of the falling-film unit) or after the adiabatic tower (in the case of the adiabatic unit). In both types of absorber units, the maintenance at all times of liquid flow adequate to wet the absorption surfaces is vital in reducing emission to the final scrubber.

Packaged commercial systems are also available for production of reagent-grade acid or anhydrous hydrogen chloride through distillation of commercial-grade 31.5% hydrochloric acid. The spent acid from such units is the azeotropic mixture (20.24% hydrochloric acid). These systems yield no emission to the atmosphere, because the manufacturing systems are closed. 88

CHAPTER 3

CONSUMPTION OF CHLORINE AND HYDROGEN CHLORIDE

CHLORINE

A recent survey prepared for the EPA Office of Air Programs[2] concluded that approximately 81.0% of the chlorine produced in 1970 was used in the production of chlorinated organic and inorganic products, about 16.0% in the pulp and paper industry, and about 3.0% in water sanitation.

Chemicals

Table 3-1 lists 16 major products to which consumption of at least 1% of the chlorine used in 1970 could be attributed. Table 3-2 lists 12 products whose manufacture required relatively minor quantities of chlorine. Subtraction of the chlorine requirements for the five inorganic chemicals in these lists (hydrogen chloride, phosgene, calcium hypochlorite, phosphorus trichloride, and sulfuryl chloride) indicates a chlorine requirement for the production of the remaining 23 organic chemicals of 67.4% of the chlorine produced in 1970, leaving a 13.6% requirement for the production of inorganic chemicals and miscellaneous other organic chemicals. For comparison, Table 3-3 lists the 1965 estimated end-use distribution of chlorine.[140]

The 14 organic major products listed in Table 3-1 consumed an estimated 64.2% of chlorine production in their manufacture in 1970.[2, 190, 227] The 23 processes involved in the manufacture of the 14 products were classified into five types, as follows:[2]

Liquid-phase chlorinations at less than 100 C and near atmospheric pressure (generally, addition reactions)--typical example:

$$Cl_2 + C_2H_4 \xrightarrow[7\ psig]{90\ C} C_2H_4Cl_2 .$$

TABLE 3-1

Major Products from Chlorine[a]

Product	Required Production of Chlorine, millions of pounds		
	1960	1970	1980[b]
Carbon tetrachloride, CCl_4	620	1,500	3,420
Chloroform, $HCCl_3$	140	450	1,460
Epichlorohydrin, C_3H_5OCl	300	500	850
Ethylchloride, C_2H_5Cl	220	300	350
1,2-Dichloroethane, $C_2H_4Cl_2$	290	2,140	7,070
Allylchloride, C_3H_5Cl	540	900	1,550
Hydrogen chloride, HCl	380	260	440
Methylchloride, H_3CCl	130	550	2,000
Methylene chloride, CH_2Cl_2	230	610	1,550
Monochlorobenzene, C_6H_5Cl	420	490	570
Phosgene, $COCl_2$	---	400	1,650
Propylene oxide, C_3H_6O	200	820	2,630
Tetrachloroethylene, C_2Cl_4	360	1,340	3,580
1,1,1-Trichloroethane, $C_2H_3Cl_3$	---	680	2,700
1,1,2-Trichloroethylene, C_2HCl_3	470	830	1,820
Vinylchloride, C_2H_3Cl	450	1,410	4,340
Total	4,750	13,180	35,980
Total chlorine production	9,280	19,500	45,500

---

[a] Derived from Air Pollution from Chlorination Processes.[2]

[b] Estimated.

TABLE 3-2

Minor Products from Chlorine[a]

Product	Required Production of Chlorine, millions of pounds 1960	1970	1980[b]
Ethylene oxide, C_2H_4O	1,845	---	---
Chloral, C_2Cl_3HO	270	140	80
Dichlorobenzene, $C_6H_4Cl_2$	180	170	240
Benzene hexachloride, C_6Cl_6	70	---	---
Calcium hypochlorite, $Ca(OCl)_2$	30	100	280
Chloroparaffins, $(C_{10}-C_{30})Cl$	10	20	60
1,2-Dichloropropane, $C_3H_6Cl_2$	15	70	210
Monochloroacetic acid, $C_2H_3O_2Cl$	40	80	130
Pentachlorophenol, C_6Cl_5OH	50	60	80
Phosphorus trichloride, PCl_3	--	100	200
Sulfurylchloride, $SOCl_2$	--	120	160
Vinylidene chloride, $CH_2=CCl_2$	--	80	---
Total	2,510	940	1,440

---

[a] Derived from Air Pollution from Chlorination Processes.[2]

[b] Estimated.

TABLE 3-3

Estimated End-Use Distribution of Chlorine, 1965[a]

End Use	Fraction of Total, %
Inorganic chemicals	9
Organic chemicals	65
Pulp and paper	17
Water and sewage treatment	4
Miscellaneous	5
Total	100

---

[a] Derived from Faith *et al.*[140]

Hydrochlorinations at less than 200 C and at 40 psig (addition reactions)--typical example:

$$HCl + C_2H_4 \xrightarrow[40\ psig]{40\ C} C_2H_5Cl.$$

Vapor-phase chlorinations at over 500 C and at 2-15 psig (generally, thermal substitution reactions)--typical example:

$$2Cl_2 + CH_4 \xrightarrow[15\ psig]{500\ C} CH_2Cl_2 + 2HCl.$$

Vapor-phase dehydrochlorinations at over 600 C and at less than 60 psig (thermal cracking reactions that drive off hydrogen chloride)--typical example:

$$C_2H_4Cl_2 \xrightarrow[50\ psig]{900\ C} CH_2{=}CHCl + HCl.$$

Vapor-phase oxychlorinations at 300 C and 75 psig, namely:

$$C_2H_4 + 2HCl + \underset{(air)}{\frac{1}{2}O_2} \xrightarrow[50-100\ psig]{300\ C} C_2H_4Cl_2 + H_2O .$$

Some dual-step processes were included in only one classification, because the products of the dual-step reactions are the only ones on which there are production data. For example, trichloroethylene is made by these two reactions:

$$2Cl_2 + C_2H_2 \longrightarrow C_2H_2Cl_4$$

and

$$C_2H_2Cl_4 \longrightarrow C_2HCl_3 + HCl.$$

The first reaction is a mild addition reaction at 50 C and atmospheric pressure, and the second is a thermal dehydrochlorination, carried out at about 600 C. There are no production figures for tetrachloroethane; therefore, trichloroethylene was placed in the fourth type, dehydrochlorination.

Other aspects of the classification were the multiple reactions that can be carried out with one raw material. Ethylene can be chlorinated, chlorohydrinated (with hypochlorous acid), or hydrochlorinated (with hydrogen chloride).

Starting with the 23 processes involved in the production of the 14 major organic chemicals, and excluding three hydrochlorination processes for production of methylchloride, ethylchloride, and vinylchloride (because no chlorine is used or produced in any stage of the processes), we are left with 20 processes with a chlorine emission potential. Of these 20 processes, the survey[2] lists 13 as having no chlorine emission factor (pounds of chlorine emitted per ton of product). Emission factors for the other seven processes were 0.0003 (for one process, chlorination of carbon disulfide), 0.001 (for two processes, chlorination of ethylene and hydrochlorination of ethylene), 0.002 (for two processes, chlorohydrination of allylchloride and then hydrolysis and chlorohydrination of propylene and then hydrolysis), and 20.0 (for two processes, thermal chlorination of propane to produce carbon tetrachloride and thermal chlorination of propane to produce perchloroethylene). With two insignificant exceptions, the emission factors listed are estimates based on little or no census or experimental information and are average values for all sources using the processes in question. In the two thermal chlorination processes listed as having a chlorine emission factor of 20.0, the source of the emission is the purge stream for removing inert materials on the dry chlorine recycle. Impurities in the process raw materials require continuous purge, but the processes are indicated to have no control system on the purge stream.

In the manufacture of inorganic chemicals, much chlorine is required for the production of synthesis hydrogen chloride, metal chlorides (including those of aluminum, zirconium, silicon and titanium),[437] bromine,[425] hypochlorites,[402] phosgene,[191] phosphorus chlorides,[496] sulfur chlorides,[314] and cyanuric chlorides.[442] There are no quantitative indications in the literature that the emission of chlorine is a problem in these operations, but it should be noted that, in general, all emission from the processes must be carefully controlled, because of the hazardous nature of the products or of the other raw materials used. Conventional vent-gas scrubbing devices based on water, alkaline solutions, or solvents are used for emission control in these processes.

Pulp and Paper

The pulp and paper industry uses four basic techniques--acid chlorination in dilute solution, alkaline hypochlorite bleaching, caustic extraction, and chlorine dioxide bleaching--in various combinations and sequences to bleach paper pulp and to purify dissolving pulps to obtain high concentrations of alpha-cellulose. The simplest bleaching sequences consist of hypochlorite only or chlorination followed by hypochlorite and are used mainly for bleaching de-inked ledger stock and de-inked stock containing some ground wood. The increased demand for pulps with higher brightness and equal or greater strength has led mills to add a chlorine dioxide stage (or stages) with or without a hypochlorite stage.

Acid chlorination is almost always the first step in bleaching wood pulp, whether for paper or for chemical cellulose.[372] The treatment consists of injecting the required quantity of chlorine gas into the unbleached stock (either directly or through a water injector), mixing chlorine and stock intimately to ensure uniform treatment of all fibers, and retaining the slurry until chlorine absorption is almost complete. Chlorination is usually carried out in an upflow tower with a retention time of 60-90 min at the prevailing tonnage rates. Improved design of chlorine water injectors, in-line mixers, and retention towers has been reported to produce savings in bleaching chemicals, either in chlorine for chlorination or in hypochlorite or chlorine dioxide for later bleaching sequences.[372] Such improved design will reduce the chlorine emission potential from the chlorination step.

Hypochlorite bleaching with either sodium- or calcium-base liquor is now almost universally carried out at high density in continuous towers--either downflow or upflow. Fully automatic, continuous systems have been developed for both sodium and calcium hypochlorite manufacture and offer many major advantages, including lower chemical costs due to complete utilization of the chlorine added.[372]

In 1962, five principal methods of generating chlorine dixoide from sodium chlorate were in use throughout the world.[372] According to Rapson,[391] a delicate balance among the rates of three fundamental reactions--

$$HClO_3 + HCl \longrightarrow HClO_2 + HClO,$$

$$HClO_3 + HClO_2 \longrightarrow 2ClO_2 + H_2O,$$

$$\text{and } HClO + HCl \longrightarrow Cl_2 + H_2O \text{ --}$$

determines the rate of production of chlorine dioxide and the ratio of chlorine to chlorine dioxide produced. Processes for chlorine dioxide generation commonly use a final 3-4% sodium hydroxide solution for absorption of the chlorine vented from the chlorine dioxide absorption tower.

Chlorine gas emission from pulp and paper mills can be controlled. In one Kraft mill bleach plant, waste gas discharges containing over 1 ton of chlorine per day were combined and scrubbed with a 4% caustic solution, with recovery of 96% of the waste chlorine as hypochlorite bleach liquor.[348] In another installation, chlorine (0.43 lb/lb of chlorine dioxide) not absorbed in the chlorine dioxide absorber solution is absorbed in dilute sodium hydroxide or injected into a flowing milk of lime solution to produce hypochlorite (the choice depends on bleach plant requirements).[401]

Water and Waste Treatment

The utility of chlorine in water treatment is attributable to its toxicologic characteristics and its oxidative capacity. Chlorine is used to destroy bacteria and other microorganisms and to modify the chemical characteristics of the water being treated. The principles of water chlorination are highlighted in Figure 3-1.[294]

An important subcategory in water treatment is the use of the toxicologic characteristics of chlorine to control fouling of heat-exchange surfaces with biologic material in fresh-water cooling circuits and to control adverse growth of marine fouling organisms in seawater cooling circuits. White[512] states that:

1. All waters--fresh or salt--are capable of growing slime on heat exchange surfaces.

2. All cooling water systems, whether for power stations, oil refineries, or other industrial uses, should be chlorinated to maintain the efficiency of the heat exchange systems.
3. No microorganism can develop a chlorine tolerance. The residual tolerance varies depending on the species.

The utility of chlorine in waste treatment is attributable to its toxicologic characteristics, its oxidative capacity, and its adaptability as a coagulant. The most important application of chlorine in sanitary waste treatment is in disinfection; alteration of physical and chemical characteristics is the most general use for chlorine in industrial waste treatment. The principles and practices of the use of chlorine in waste treatment are highlighted in Figure 3-2.[293]

Laubusch[293, 294] and White[512] have dealt extensively with the need to consider chlorination equipment in the water and waste treatment as a total system to include the following elements:

> Sufficient equipment for adequate dosage (dual, standby systems should ordinarily be provided in community water supply operations to protect the public health).
>
> Proper rapid mixing at the point of application.
>
> Suitable contact chamber after rapid mixing, giving a distribution of contact time approaching the ideal time of unity (ideal plug flow).
>
> Continuous residual control of the chlorine metering equipment based on the amperometric method of residual determination.

Final monitoring of residual chlorine at the end of chlorine contact time.

Appropriate alarm functions to warn of malfunction in the total system and safety interlocks for automatic shutdown.

Although this publication lists a chlorine-emission accident in an American filtration plant in 1969 that caused two fatalities and a chlorine-emission accident in an American swimming pool in 1971 that was serious (although it caused no fatalities), the dearth of such reported incidents indicates that emission of chlorine from water and waste treatment operations does not constitute a significant environmental problem.

HYDROCHLORIC ACID (100% BASIS)

Table 3-4 lists two estimated end-use distribution patterns for hydrochloric acid (100% basis).

TABLE 3-4

End-Use Distribution of Hydrochloric Acid (100% Basis)

	Fraction of Total, %	
End Use	1965[a]	1971[b]
Chemicals	51	33
Metals industry	21	47
Food-processing	9	7
Oil-well acidizing	7	6
Miscellaneous	12	7
Totals	100	100

---

[a] Data from Faith *et al.*[140]

[b] Data from *Chemical Briefs*.[234]

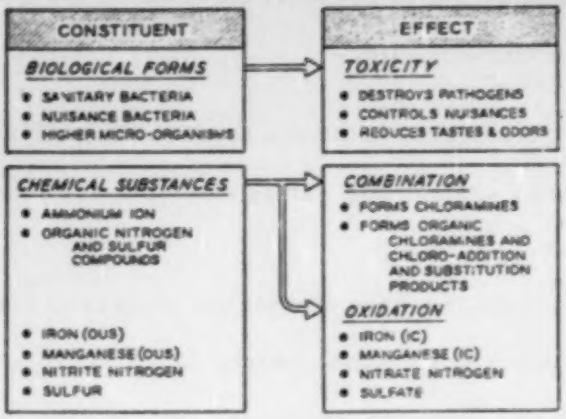

CONSTITUENT
EFFECT
BIOLOGICAL FORMS
• SANITARY BACTERIA
• NUISANCE BACTERIA
• HIGHER MICRO-ORGANISMS
TOXICITY
• DESTROYS PATHOGENS
• CONTROLS NUISANCES
• REDUCES TASTES & ODORS
CHEMICAL SUBSTANCES
• AMMONIUM ION
• ORGANIC NITROGEN AND SULFUR COMPOUNDS
• IRON (OUS)
• MANGANESE (OUS)
• NITRITE NITROGEN
• SULFUR
COMBINATION
• FORMS CHLORAMINES
• FORMS ORGANIC CHLORAMINES AND CHLORO-ADDITION AND SUBSTITUTION PRODUCTS
OXIDATION
• IRON (IC)
• MANGANESE (IC)
• NITRATE NITROGEN
• SULFATE

FIGURE 3-1. Principles of water chlorination. (Reprinted with permission from Laubusch.[294])

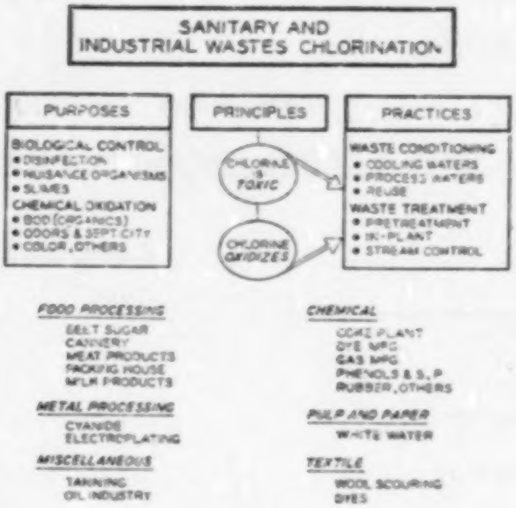

SANITARY AND INDUSTRIAL WASTES CHLORINATION
PURPOSES
PRINCIPLES
PRACTICES
BIOLOGICAL CONTROL
• DISINFECTION
• NUISANCE ORGANISMS
• SLIMES
CHEMICAL OXIDATION
• BOD (ORGANICS)
• ODORS & SEPTICITY
• COLOR, OTHERS
CHLORINE IS TOXIC
CHLORINE OXIDIZES
WASTE CONDITIONING
• COOLING WATERS
• PROCESS WATERS
• REUSE
WASTE TREATMENT
• PRETREATMENT
• IN-PLANT
• STREAM CONTROL
FOOD PROCESSING
BEET SUGAR
CANNERY
MEAT PRODUCTS
PACKING HOUSE
MILK PRODUCTS
METAL PROCESSING
CYANIDE
ELECTROPLATING
MISCELLANEOUS
TANNING
OIL INDUSTRY
CHEMICAL
COKE PLANT
DYE MFG
GAS MFG
PHENOLS & S. P
RUBBER, OTHERS
PULP AND PAPER
WHITE WATER
TEXTILE
WOOL SCOURING
DYES

FIGURE 3-2. Typical applications of chlorine in waste treatment for resource conservation and pollution abatement. (Reprinted with permission from Laubusch.[293])

It should be recognized that accurate national end-use consumption tonnages for hydrochloric acid (100% basis) are difficult to estimate and that few of the attempts at estimation are published. Attempts to estimate end-use consumption tonnages from reported production or shipment figures (including interplant transfers) are subject to error, because the reported shipment figure for each year since 1947 has represented less than 50% of the reported production figure for the corresponding year.[235] In addition, actual production of byproduct hydrochloric acid (100% basis) is considerably in excess of what is recovered and reported,[235] and the disposition of the unreported production from the dominant byproduct processes is unknown. Unusual regional supply-and-demand situations for hydrochloric acid (100% basis) tend to confuse the national end-use consumption picture further. Finally, end-use consumption tonnage estimation for hydrochloric acid (100% basis) is made more difficult, because of the many chlorination processes wherein anhydrous hydrogen chloride is used in conjunction with or as a substitute for chlorine.

Anhydrous hydrogen chloride in hydrochlorination reactions leading to ethylchloride, methylchloride, vinylchloride, 1, 1, 1-trichloroethane, and 1, 1, 1-trichloroethylene and in oxychlorination reactions leading to vinylchloride and trichloroethylene has dominated the use of hydrochloric acid (100% basis) in the production of organic chemicals. Another significant use for anhydrous hydrogen chloride is in the production of chloroprene, the monomer for production of neoprene. Potential hydrogen chloride gas emission from such processes has been discussed in Chapter 2.

The aqueous acid is used in the production of dyes and dye intermediates, in the preparation of chlorides from alcohols, as a catalyst in organic reactions, in the preparation of pesticides, and in the preparation of pharmaceutical-grade chemicals, such as adipic acid, citric acid, amine hydrochlorides, and aconitic acid.[276] The use of the aqueous acid has grown tremendously in the metal and industrial cleaning field, but particularly in steel-pickling applications.[235] Since 1964, a large percentage of the steel companies in the United States have switched to hydrochloric acid using the conventional horizontal pickling baths after minor modification. Inhibited hydrochloric acid is also used for the removal of sludge and hard-water scale from boilers, heat exchangers, pipes, and other industrial equipment. Oil-well acidizing operations use a large tonnage of inhibited hydrochloric acid to dissolve subsurface limestone or dolomite formations, thereby decreasing the resistance to oil or gas flow.[235] Finally, hydrochloric acid is used in a host of other applications, ranging from the extraction and processing of minerals to the hydrolysis of proteins and starch and reactivation of bone char and charcoal in sugar refining.[276]

Emission of hydrogen chloride gas from industrial operations that use hydrochloric acid is not judged to be a significant atmospheric pollution problem, because of the strong affinity of the gas for water. Depending on such factors as the strength of acid, the temperature of use, the type of equipment, the local ventilation, and the emission control devices, various problems of environment control and corrosion control are encountered. Equilibrium pressures of hydrogen chloride increase markedly with temperature, especially over acid solutions containing more than 20% hydrogen chloride; equilibrium pressures over dilute acid (under 20%) may be considered negligible.[276]

CHAPTER 4

ATMOSPHERIC CHEMISTRY OF CHLORINE COMPOUNDS

ATMOSPHERIC CHEMISTRY OF NATURAL CHLORINE COMPOUNDS

Natural Atmospheric Chlorides

Particles. The ocean is the primary natural source of chlorine present in particles (hereafter referred to as particulate chloride) in the atmosphere. There is good evidence of a direct relationship between the gaseous chlorine compounds in nonurban air and atmospheric sea salt particles. Most of the sea salt particles that remain in the atmosphere longer than a few minutes are produced by the breaking of bubbles at the sea surface. These bubbles may be formed by breaking waves and by raindrops and snowflakes that strike the water surface. Except under some local conditions, breaking waves (whitecaps) are by far the most important source.

The mechanism of salt particle injection into the atmosphere by bursting bubbles has been studied extensively and is reviewed in detail by Blanchard.[42] There have been only two detailed attempts to estimate the annual global production of atmospheric sea salt particles, those of Eriksson[133] and Blanchard.[42] Both authors determined the production rate by calculating the amount of salt removed from the atmosphere by precipitation and dry fallout, making various assumptions as to the particle concentrations in the atmosphere, the effective particle deposition velocity, the strength of the wind (which affects the atmospheric particle number and size distribution), and the average salt content of rainfall. The two estimates disagree by a factor of about 9, Blanchard estimating a salt production of 10×10^{12} kg/year, and Eriksson, 1.1×10^{12} kg/year. Eriksson's estimate has been quoted commonly, and his figure is generally used for the annual sea salt production,[209,238,400] but Blanchard's calculation appears equally reasonable and must also be considered. Thus, the best estimates are that the sea salt production is 1.1-10 x 10^{12} kg/year and results in a particulate chloride production of 0.7-6 x 10^{12} kg/year, as shown in Table 4-1. Approximately 90% of this is returned to the ocean surface, and 10% is deposited on the continents.

There have been a number of estimates of the global injection of soil and rock weathering products into the atmosphere, ranging from 7 to 500 x 10^{9} kg/year.[178, 209, 325, 378, 400] According to Mason,[325] chlorine accounts for about 0.02% of the mass of crustal rocks. Applying this figure the various estimates result in a range of global annual production of particulate chloride from crustal weathering of only 0.0014-0.10 x 10^{9} kg (as shown in Table 4-1)--far less than oceanic production.

Estimates of the production of atmospheric particles by volcanoes vary from 4 x 10^{9} kg/year[209, 400] to 25 x 10^{9} kg/year[378] (there is even one estimate of 150 x 10^{9} kg/year.[178] Assuming an average chlorine content of igneous rocks of 0.032%[507] results in a chloride production estimate of 0.0013-0.008 x 10^{9} kg/year in particles from volcanoes--again far less than oceanic production.

Almost no quantitative data are available on the production of atmospheric particles by forest fires. Estimates of particle production range from 3 to 150 x 10^{9} kg/year.[209, 400] Chemical analysis of forest fire particles are also lacking, but even an assumption that 1% of the particulate mass is chloride--a very high value--results in a maximal particulate chloride production from forest fires of only 1.5 x 10^{9} kg/year.

Gases. There has been considerable controversy concerning the source of the natural gaseous chlorine species present in the atmosphere. Duce[113] has reviewed the various arguments in this problem. It has not been determined what chemical species of chlorine are present in the gas phase in the undisturbed

TABLE 4-1

NATURAL SOURCES OF ATMOSPHERIC PARTICULATE CHLORIDE

Source	Estimated Production Rate, 10^9 kg of Chloride per Year
Sea salt	700-6,000
Crustal weathering	0.0014-0.10
Volcanoes	0.0013-0.008
Forest fires	<<1.5

atmosphere. Two sources have been suggested for gaseous chloride in uncontaminated air: sea salt particles and volcanism.

The most commonly accepted view is that the gaseous chlorine constituents found in uncontaminated marine air are released from sea salt particles. A number of reactions have been suggested that would result in this release.

Sea salt particles exist as saline droplets in the atmosphere at relative humidities above 70%. Over the sea, the relative humidity in the lower few hundred meters of the atmosphere averages 70-80%. Even at lower humidities, these particles are surrounded by a thin envelope of water. Cauer[68] suggested that the aqueous chloride in aerosol particles reacts with ozone to form chlorine, which later escapes from the particles. He envisioned the reactions as:

$$O_{3(g)} + Cl^-_{(aq)} \longrightarrow O_{2(g)} + ClO^-_{(aq)} \qquad (1)$$

and

$$ClO^-_{(aq)} + 2H^+_{(aq)} + Cl^-_{(aq)} \longrightarrow Cl_{2(g)} + H_2O_{(l)}. \qquad (2)$$

These reactions were studied in detail by Yeatts and Taube,[526] who found Eq. 1 to be rate-determining. Eriksson[134] points out that, on the basis of Yeatts and Taube's rate measurements, it would take several thousand years for the chloride in sea salt particles to be converted to hypochlorite with the concentrations of ozone normally found in nonurban air, although the conversion may be 10-100 times faster in urban air, with higher oxygen concentrations. This suggests that chloride oxidation by ozone is probably not a major mechanism of release of gaseous chlorine compounds from atmospheric sea salt. In addition, Zafiriou[527] has pointed out that chlorine would probably undergo relatively rapid photolysis in the atmosphere, with the ultimate product possibly being hydrogen chloride.

Eriksson[134] believed the gaseous chlorine compound in marine air was hydrogen chloride released from sea salt particles. He suggested that sulfur trioxide, formed by the oxidation of sulfur dioxide, dissolves in the particles, lowering the pH and releasing hydrogen chloride. The following must be considered:

$$\mathrm{HCl}_{(aq)} \longrightarrow \mathrm{HCl}_{(g)} \;; \qquad K = 10^{-6.4} \;. \tag{3}$$

The pressure of hydrogen chloride (pHCl) in equilibrium with the saline droplets is given by

$$\mathrm{pHCl} = 10^{-6.4}\, a_{H^+} \cdot a_{Cl^-} \;. \tag{4}$$

The chloride concentration will vary from the seawater value, 0.55 M, to a maximum of about 6-7 M at low humidities, and the activity coefficient for chloride will be approximately 0.7. If all the gaseous chlorine species are present as hydrogen chloride, its partial pressure in the atmosphere is about

10^{-9} atm. (See also the following section). According to Eq. 4, the equilibrium pH of the sea salt particles would vary from 2.2 (for 0.55 M chloride to 3.3 (for 7.0 M chloride). These pH values appear rather low for sea salt particles. Junge[254] has pointed out that the ammonia concentration in the marine atmosphere is sufficient to keep the pH higher. Blanchard[41] has shown, however, that there are approximately equal amounts of chloride and surface-active organic film material in sea salt particles in the marine atmosphere. The presence of this organic material as a compressed film on the surface of a particle would probably influence the transfer of gaseous species across the droplet surface, and it is possible that simple considerations of ionic equilibria are not valid in this situation.

It has also been suggested that nitrosylchloride, NOCl, may be the initial form of gaseous chlorine in marine air. Junge[258] found that the nitrate content of sea salt particles in coastal areas of the northeastern United States was greatest for the giant particles, those containing most of the chloride. He further determined that the presence of nitrate in the aerosols depended on the presence of both nitrogen dioxide and sea salt particles. On the basis of Junge's results, Robbins _et al._[398] studied the following reactions:

$$NaCl_{(s)} + 2NO_{2(g)} \longrightarrow NaNO_{3(s)} + NOCl_{(g)} \qquad (5)$$

and

$$NOCl_{(g)} + H_2O_{(l)} \longrightarrow HCl_{(g)} + HNO_{2(l)} . \qquad (6)$$

The reaction of Eq. 5 with bulk moist sodium chloride was slow, but complete--i.e., all the nitrogen dioxide was reacted. With sodium chloride aerosols, however, the reaction was rather rapid, but incomplete; the authors suggested that that ruled out Eq. 5. Also, any nitrosylchloride formed should be rapidly hydrolyzed according to Eq. 6, giving hydrogen chloride and nitrite as final products. Junge[258] however, had found no nitrite in his analyses.*

Robbins et al.[398] then suggested that nitrogen dioxide is hydrolyzed in the gas phase,

$$3NO_{2(g)} + H_2O_{(g)} \longrightarrow 2HNO_{3(g)} + NO_{(g)}, \qquad (7)$$

and the nitric acid, HNO_3, is later dissolved in the sea salt droplets. They found that, with the excess water available, about 5% of the nitrogen dioxide was converted to nitric acid. The decrease of the sea salt particle pH on dissolution of the nitric acid would result in the release of hydrogen chloride according to Eq. 3. This explanation, however, suffers from the same problem as the sulfur trioxide mechanism: it appears unlikely that the pH can become low enough on the particles for the particles to be in equilibrium with the gaseous chlorine compounds observed in the marine air, assuming that the chlorine is present as hydrogen chloride. Thus, it is clear that, if the gaseous chlorine compounds in marine air comes from salt particles, strict ionic thermodynamic considerations, such as those above, cannot describe the situation adequately.

Petriconi and Papee[380] have suggested that highly reactive transient pernitrite intermediate oxidants can be formed photolytically in saline solutions that contain nitrate and that these strong oxidizing agents may result in the release of halogen-containing gases from seawater and atmospheric sea salt particles. It is very likely that photochemical reactions play an important role in the chemistry of atmospheric chlorine compounds.

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* Recent work by Schroeder and Urone[414a] with sodium chloride particles and nitrogen dioxide showed that Eq. 5 proceeds rapidly, but depends on surface area. They suggest that this may be an important source of atmospheric nitrosylchloride. More work is clearly needed on this subject.

If gaseous chlorine in some form is released from atmospheric sea salt particles, the chloride:sodium ratio on the particles should be lower than that in seawater, which is 1.80:1. Unfortunately, and surprisingly, very little information is available on the chloride:sodium ratio in marine aerosols. Junge[258] found a mean atmospheric chloride:sodium ratio of (1.79 ± ?):1 along the Florida coast. Chesselet et al.[74] found that the ratio in particles collected over the North Atlantic was (1.72 ± 0.03):1, suggesting a chlorine loss of 4-5%. The mean ratio found on sea salt particles in Puerto Rico by Martens et al.[324] was (1.57 ± 0.16):1, suggesting a gaseous chloride loss of approximately 13%. Wilkniss and Bressan[516] measured the ratio on particles collected from surface air over the Atlantic and Pacific. They found a mean ratio of (1.88 ± 0.34):1 for particles ≥ 2 μm in radius and (1.40 ± 0.26):1 for all particles ≥ 0.2 μm in radius. The latter figure would represent about a 22% chloride loss, and their results suggest that the chloride loss is from the smaller particles. These studies indicate that there may be a 5-20% loss of chloride on sea salt particles relative to the chloride:sodium ratio in seawater.

Martens et al.,[324] Wilkniss and Bressan[516] and Rahn[389] investigated the variation in the chloride:sodium ratio with particle size. Wilkniss and Bressan, in laboratory bubbling experiments, found a depletion in the ratio relative that in seawater on the smallest particles collected (radius, ≤ 0.4 μm). Martens et al. found a very pronounced tendency toward chloride loss from the smallest sea salt particles collected in ambient air both in Puerto Rico and in the San Francisco Bay area. This chloride loss from the smallest particles was also noted by Rahn at inland sites in northern Canada. Martens et al. found that chloride losses from the particles were approximately inversely proportional to the particle radius, with over 90% of the chloride on the smallest particles (radius 0.2-0.4 μm) lost and less than 10% of the chloride on the largest particles (radius, > 5 μm) lost. They suggest that the chloride loss may be controlled by a gain of hydrogen ion, which depends on particle surface area.

A few recent observations at a remote location off the shore of southern California have shown anomalously high chloride:sodium ratios in aerosols. On the basis of aerometric and meteorologic considerations, Hidy *et al.*[210] have argued that anthropogenic sources cannot be responsible for these high ratios. They have speculated that there may be a connection between removal of hydrogen chloride by absorption into aged aerosols in the middle and upper troposphere and the material that reaches the surface of the western Pacific from large-scale subsidence of air around the Pacific high-pressure area. Their arguments are supported by Gillette and Blifford's evidence[170] of increasing chloride:sodium ratio with altitude over the Pacific Ocean.

In the relatively polluted San Francisco Bay area, Martens *et al.*[324] showed that there was a relationship between gaseous nitrogen dioxide and absolute chloride loss from the particles calculated from the chloride:sodium ratio for the total particle distribution. They suggest that this supports the second hypothesis of Robbins *et al.*,[398] i.e., Eq. 7. Their data indicate a loss of about 0.06 micromole of chloride per standard cubic meter (SCM) for every micromole of nitrogen dioxide. If the chloride loss is a result of nitric acid interaction, the amount of nitric acid taken up by the particles would represent about 6% of the available nitrogen dioxide.

In Puerto Rico, Martens *et al.*[324] found a relatively constant chloride loss from the sea salt particles, about 0.006 micromole/SCM. Assuming a natural background nitrogen dioxide concentration of 0.04-0.07 micromole/SCM[254] and assuming that 6% of this nitrogen dioxide were converted to nitric acid and taken up by the aerosol, approximately 0.002-0.004 micromoles of hydrogen ion per standard cubic meter could be supplied to the particles. This is about half that required to balance the loss of chloride. The authors point out that sulfur dioxide conversion to sulfuric acid may also be important in explaining the overall chloride loss that they found in Puerto Rico.

Volcanoes have also been suggested as a source of gaseous chlorine in uncontaminated air. Valach[495] believed that the amount of hydrogen chloride released from sea salt owing to the dissolving of sulfur trioxide in the particles could not account for the total gaseous chlorine observed in the atmosphere. He based this belief primarily on the fact that, in general, the chloride:sodium ratio on bulk particles is only 50-20% below the ratio in seawater, and he held that the sulfate:sodium ratio is not sufficiently above the seawater value to account for the amount of gaseous chlorine observed in air, which is approximately half the particulate chlorine concentration in the lower troposphere. Valach did not consider the possibility of nitric acid addition to the particles. He suggests that the gaseous chlorine is hydrogen chloride, but that only 10-20% of it could be from sea salt, with the rest volcanic in origin.

Eriksson[134] estimated the total worldwide volcanic production of gaseous chloride to be 9×10^{9} kg/year, a figure with which Valach agreed. Much of this gaseous chloride probably goes directly into local groundwater or the ocean. Assuming that 15% of the particulate chloride produced by the ocean is converted to gaseous chloride results in an estimate of global production gaseous chlorine from sea salt particles of $1\text{-}9 \times 10^{11}$ kg/year. Thus, apparently, less than 10% of the gaseous chloride is volcanic in origin.

The relative importance of other natural sources of gaseous chloride is unknown. Such sources could include forest and grass fires and acidic soils, especially near coastal areas, which might release hydrogen chloride.

Until the magnitudes of these and the previously discussed sources are determined with some precision, there will continue to be large uncertainties in our understanding of the natural cycle of chloride compounds between the earth, the atmosphere, and the oceans.

Natural Background Concentrations in Remote Locations

Particles. There have been numerous measurements of the concentration of salt particles in marine air. Some of the most extensive studies have been made by Woodcock in Hawaii. Figure 4-1 shows a typical number distribution of sea salt particles of different weights and sizes in the marine atmosphere at various wind forces in Hawaii.[521] It is apparent that both the number of particles and their upper size limit increase with increasing wind speed. This is a direct result of increased wave action and bubble formation. These results were confirmed by Lodge[306] in Puerto Rico. With improved collection techniques, Woodcock[522] has recently extended his studies to show that salt particles as small as 0.01-0.001 picogram (pg), with radii of 0.2-0.2 μm at 90% R.H., are present in marine air. With normal fair-weather wind speeds of 3-10 m/sec, the average particulate chloride content of marine air is 1-10 μg/SCM.

Toba[478,479] and Durbin and White[121] have made detailed studies of the vertical distribution of sea salt particles over the ocean. Toba finds that the salt content generally decreases exponentially with altitude. In the tropics, the atmospheric concentration of sea salt 3,000 m over the ocean is only about 1% of its concentration near sea level.[478] This rapid decrease is probably due primarily to very effective washout of these hygroscopic particles in convective clouds and low-pressure storms.[257]

Sea salt particles penetrate to the interior of continental regions, although their concentration near the land surface decreases rapidly as one moves inland, and it is often difficult to distinguish between chloride present

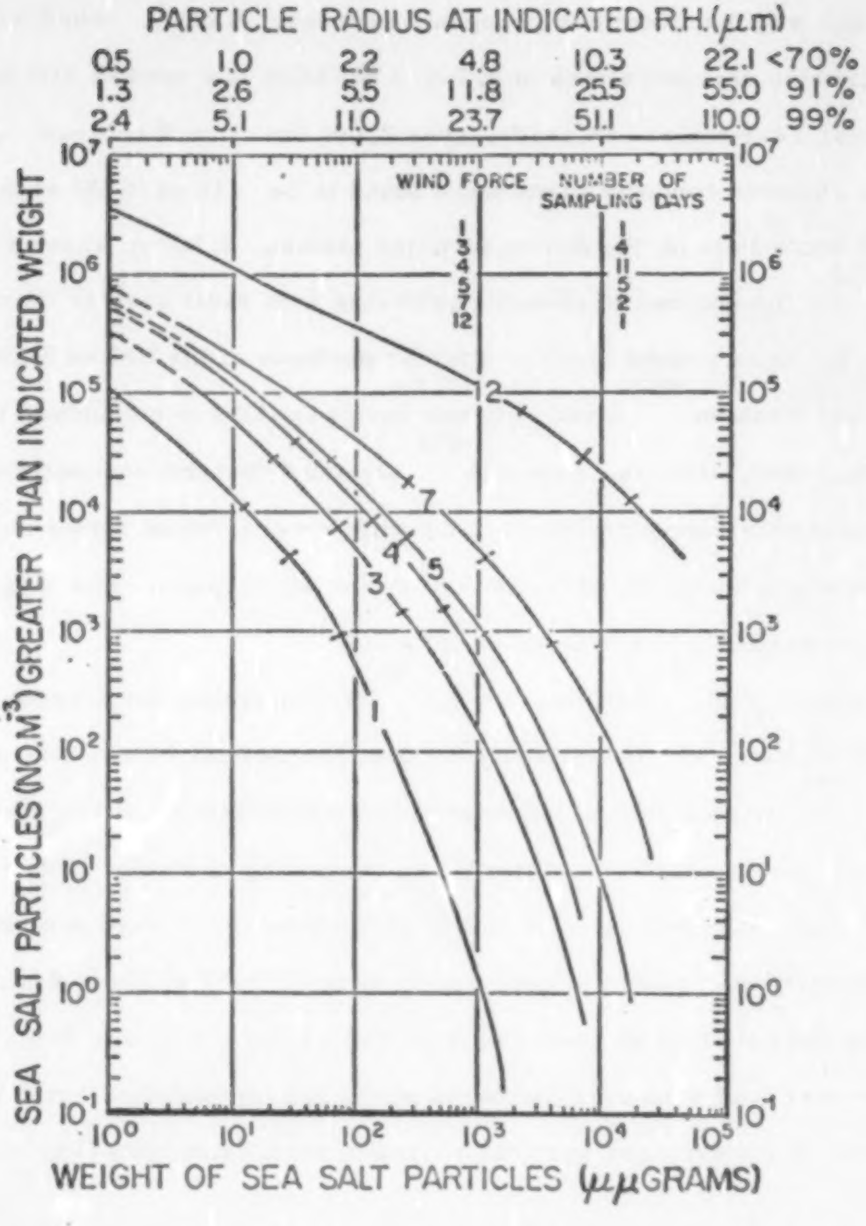

FIGURE 4-1. Number and weight of sea salt particles 800-1,000 m over the ocean near Hawaii as a function of wind force. Three short transverse lines on each curve mark the first quartile, median, and third quartile weight distribution points. (Derived from Woodcock.[521])

in sea salt and that from anthropogenic sources. Rahn[389] found surface level chloride concentrations of 0.1-0.3 μg/SCM at a remote site in the Northwest Territories in Canada, over 2,000 km from the ocean. Atmospheric chloride concentrations were found to be < 10 ng/SCM at the geographic South Pole on the Antarctic polar plateau, 2,800 m above sea level.[118] The number of chloride particles with radii greater than 10 μm is very low near ground level in interior portions of the United States. Reitan and Braham[394] found only two such particles per standard cubic meter in central Illinois. Semonin[418] reported that the concentrations of the largest chloride particles over the midwestern United States showed no clear relationship to the advection of marine air masses, thus suggesting that these particles are nonmarine in origin.

Crozier *et al.*[97] and Byers *et al.*[61] demonstrated the presence of sea salt particles at various altitudes over the central United States, and Twomey[484] made a similar study over central Australia. Byers *et al.* found that the concentration of particles containing chloride with radii greater than 3μm increased in the first few hundred meters over the land and then was relatively constant up to an altitude of about 4 km. The concentration of chloride particles with radii over 3μm was actually greater over land than over the ocean above approximately 2 km. This is the result of the stronger vertical mixing of the atmosphere over land areas.

Gases. There are very few measurements of gaseous chlorine species in the uncontaminated atmosphere. Junge[255,258] measured gaseous chloride in coastal regions of Florida and Hawaii, Duce *et al.*[116] in Hawaii, and Chesselet *et al.*[74] and Buat-Menard[56] over the North Atlantic Ocean and in coastal areas of western France. The atmospheric concentrations observed by these authors are summarized in Table 4-2. The mean sea-level gaseous

TABLE 4-2

Gaseous and Particulate Chloride in the Marine Atmosphere

Location	Gaseous Chloride concentration, μg/SCM		No. samples	Particulate Chloride concentration, μg/SCM		No. samples	Gas:Particle Ratio
	Mean	Range		Mean	Range		
Florida, coastal[258]	2.2	?	7	2.4	?	7	0.9:1
Hawaii, coastal[255]	2.2	1.0-3.4	11	5.1	2.5-12.3	8	0.4:1
Hawaii, coastal[116,350]	3.7	0.3-6.5	6	4.5	2.3-7.0	11	0.8:1
North Atlantic,[56] sea level	3.4	1.6-11.6	20	14.5	2.6-43.8	15	0.2:1
Hawaii, 3,000 m[255]	1.0	0.8-1.4	6	<0.1	-	2	>100:1
Hawaii, 3,500 m[116]	2.0	0.8-3.1	3	∿0.1	-	1	∿ 20:1

chlorine (as chloride) concentrations found vary from 2 to 4 μg/SCM. These results are in remarkable agreement and suggest that the gaseous chloride concentration is much less dependent on such factors as wind speed and precipitation than is particulate chloride. This again supports a longer residence time of gaseous chloride. The gaseous chloride concentration decreases by a factor of about 2 from the surface to 3,000 m in Hawaii.

The ratio of gaseous to particulate chloride measured at sea level ranges from 0.2:1 to 0.9:1 (Table 4-2). The variation in this ratio is determined largely by the variation in the particulate concentration, which depends heavily on wind speed, collection of local spray, rainfall, elevation, etc. As an average, however, it appears that the gaseous chloride concentration is about half the particulate concentration near sea level. The measurements at 3,000 and 3,500 m above sea level show that the gaseous chloride concentration is at least 20 times the particulate concentration at those elevations.

Precipitation. The chloride content of precipitation in uncontaminated air has been investigated primarily in the marine environment. Concentrations of chloride in rain at sea level range from a few tenths of a milligram to tens of milligrams per liter, depending on wind speed and sea state. Junge[254] summarized the results of many analyses of rainwater for chloride before 1962. The chloride content of rain decreases with altitude and distance from the coast in Hawaii,[116] with a mean concentration of about 7 mg/liter at sea level decreasing to 0.15 mg/liter at an altitude of 2,200 m (a distance of 40 km inland). The chloride concentration also varies inversely with rainfall intensity.[114,132,159,256,483,523]

The chloride:sodium ratio in rain in marine air is generally at or slightly below the seawater ratio of 1.80:1.[134,259,420] Duce et al.[114] showed that the ratio does not vary appreciably with rainfall intensity or raindrop size.

In continental areas, the chloride content of precipitation decreases rapidly as one moves away from the coast. This is shown clearly in Figures 4-2 and 4-3, which present the results of the analyses of rain samples collected in the United States.[259, 307]

The geographic distribution of chloride:sodium ratios also is instructive in showing the influence of urban areas on total atmospheric chloride content. Figure 4-4 shows the ratios for 1960-1966 based on data from the U.S. National Precipitation Network.[307] The ratio is 1.8 for seawater, and it can be seen that in only a few places is the ratio much larger--mainly in the Midwest and in upper New York state. It is interesting that analysis of earlier rainwater data failed to display such high ratios in large urban areas (e.g., Junge and Werby[259]).

Relation of Chlorine to Other Halogens in the Natural Atmosphere

Bromine. Analysis of atmospheric particles in marine air for bromide and chloride has shown that the bromide:chloride ratio in these particles collected over the ocean or on the coast is somewhat lower than the seawater ratio of 0.0034:1. Duce *et al.*[116,117] and Moyers and Duce[349] found the ratio on particles collected in these regions of Hawaii to range from 0.0005:1 to 0.003:1, with an average of about 0.002:1. However, rain collected inland in Hawaii showed ratios that were roughly twice the seawater ratio.

Duce *et al.*[117] and Moyers and Duce[349] measured the bromide and chloride concentrations in different-size particles in Hawaii and used a cascade impactor for particle collection. The total particulate bromide concentration was about 9 ng/SCM. The variations in chloride and bromide concentrations and bromide:chloride ratio for 12 impactor samples are shown in Figures 4-5 and 4-6. The shape of the size distribution curve is similar for the two elements; the bromide:chloride ratio tends to be lower for intermediate particle

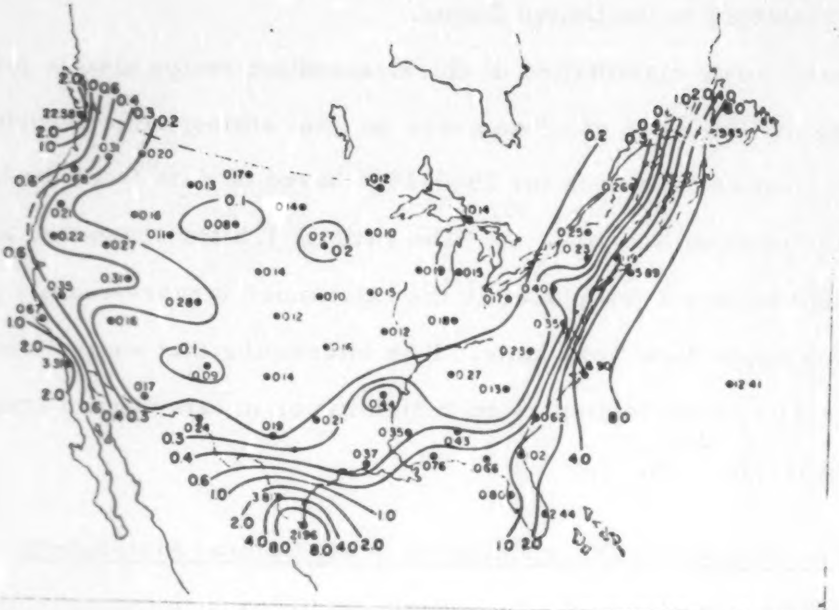
2.0
0.6
0.4
0.3
0.2
22.38
2.0
1.0
0.31
0.20
0.6
0.68
0.17
0.13
0.12
0.1
0.08
0.14
0.21
0.16
0.11
0.22
0.27
0.27
0.2
0.10
0.14
0.14
0.6
0.31
0.35
0.28
0.10
0.15
0.19
0.15
0.17
0.67
1.0
0.16
0.12
0.12
0.18
2.0
0.1
0.16
3.31
0.09
0.14
0.27
0.23
0.13
2.0
0.17
0.6
0.4
0.3
0.24
0.19
0.21
0.44
0.3
0.4
0.35
0.43
0.62
0.37
0.76
0.66
1.02
0.6
1.0
3.81
0.80
1.0
2.0
21.96
4.0
8.0
8.0
4.0
2.0
2.44
1.0
2.0
0.2
1.0
2.0
4.0
8.0
0.4
0.3
3.85
0.26
0.25
0.23
0.40
0.35
1.19
5.89
6.90
12.41
8.0
4.0

FIGURE 4-2. Average chloride concentration in rainfall over the United States, in milligrams per liter, July 1955-June 1956 (Reprinted with permission from Junge and Werby, 1958).[259]

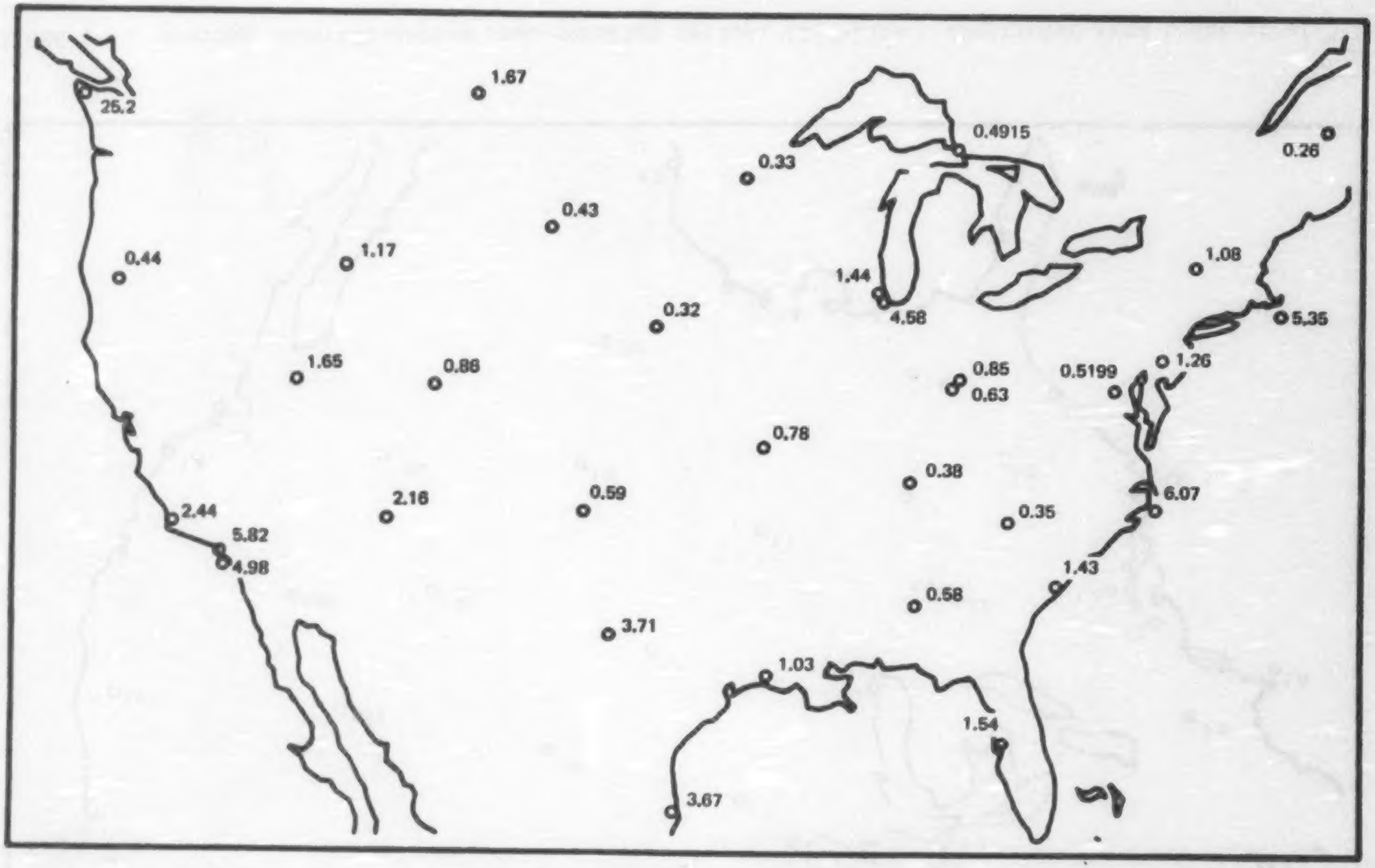
1.67
25.2
0.4915
0.26
0.33
0.43
0.44
1.17
1.08
1.44
4.58
0.32
5.35
1.65
0.88
0.85
0.63
0.5199
1.26
0.78
0.38
2.16
0.59
6.07
2.44
0.35
5.82
4.98
1.43
0.58
3.71
1.03
1.54
3.67

FIGURE 4-3. Average chloride concentration in rainfall over the United States, in milligrams per liter, 1960-1966. (Reprinted from Lodge et al.[307])

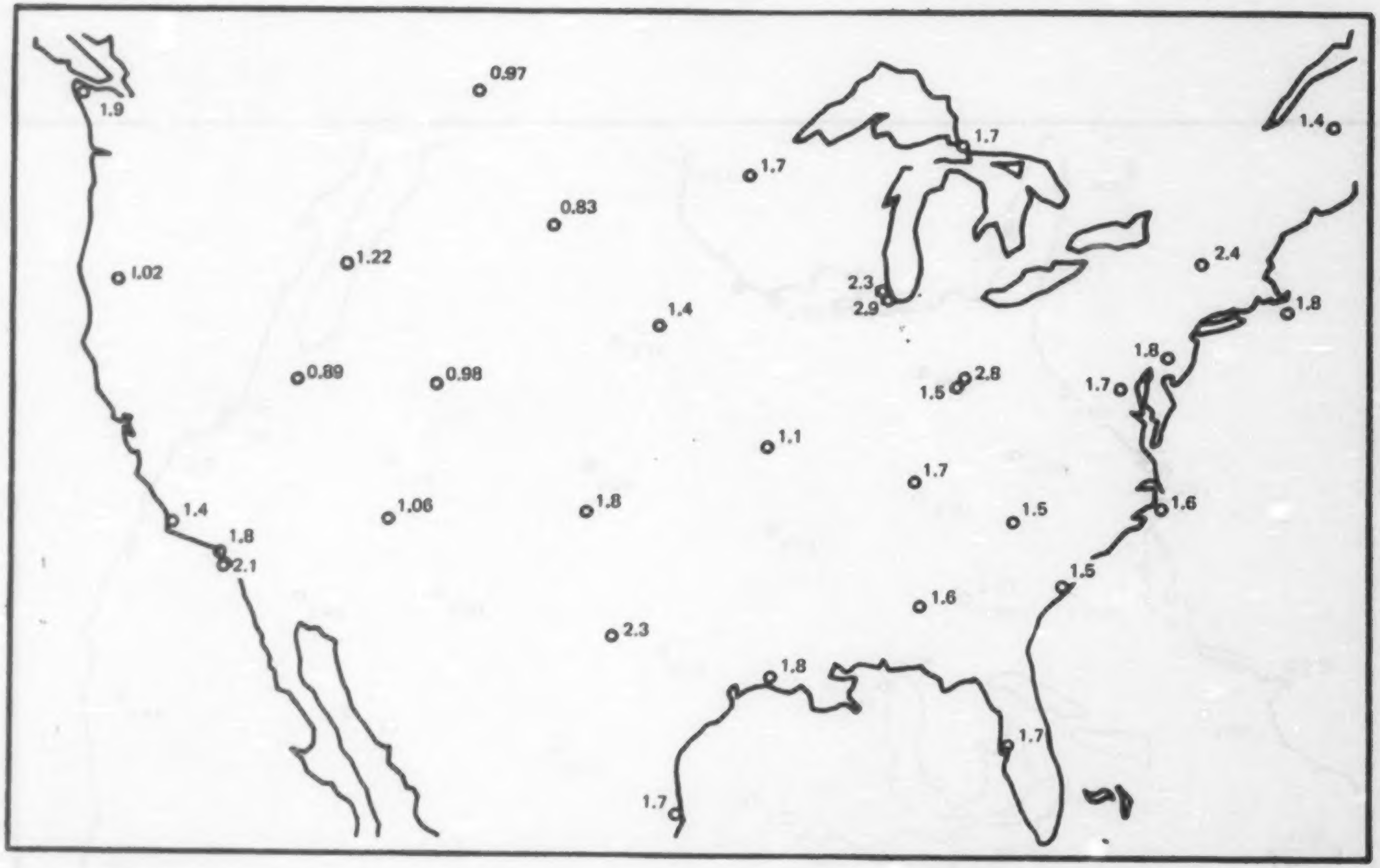
1.9
0.97
1.7
1.7
1.4
1.02
1.22
0.83
2.4
2.3
2.9
1.4
1.8
0.89
0.98
1.8
2.8
1.7
1.5
1.1
1.7
1.4
1.06
1.8
1.5
1.6
1.8
2.1
1.5
1.6
2.3
1.8
1.7
1.7

FIGURE 4-4. Average chloride:sodium concentration ratios, 1960-1966. (Reprinted from Lodge et al.[307])

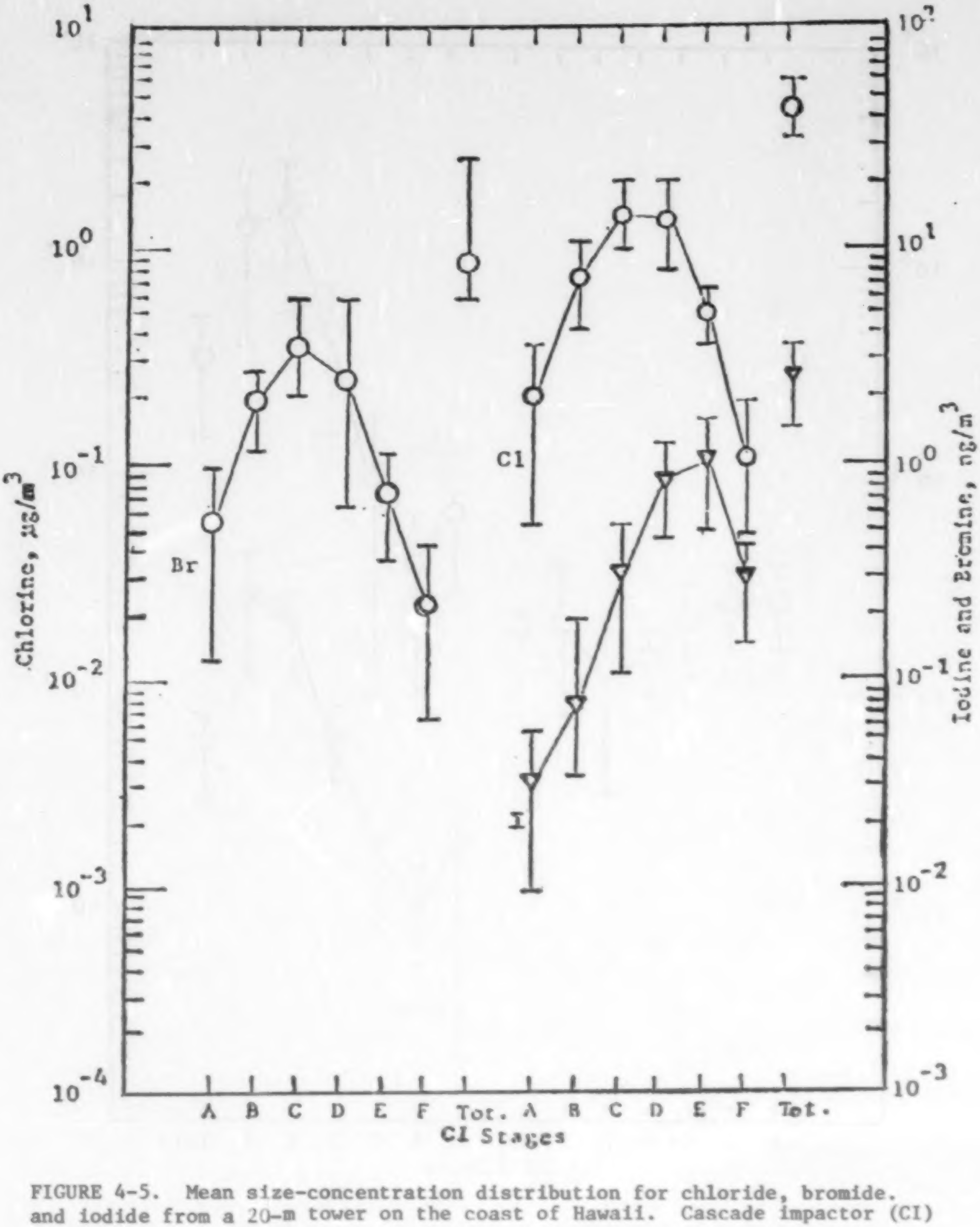

FIGURE 4-5. Mean size-concentration distribution for chloride, bromide. and iodide from a 20-m tower on the coast of Hawaii. Cascade impactor (CI) stages A-F have approximately 100% collection efficiencies for particles of >10 µm on stage A, 5 µm on stage B, 2.5 µm on stage C, 1.2 µm on stage D, 0.6 µm on stage E, and 0.3 µm on stage F. Tot., total concentration for all sizes collected. (Derived from Moyers and Duce.[349,350])

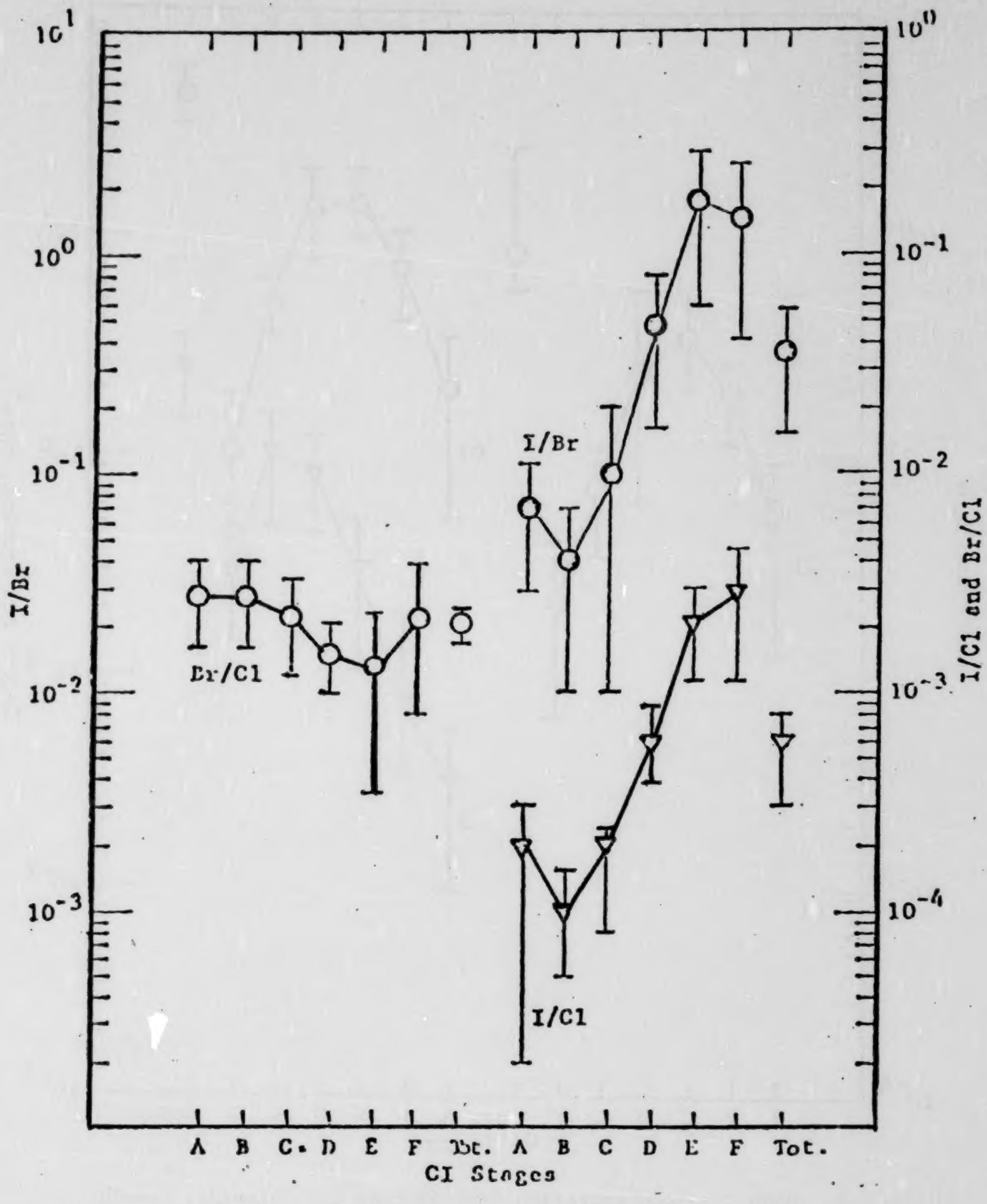

FIGURE 4-6. Mean halogen ratio variation with particle size for particles collected from a 20-m tower on the coast of Hawaii. See Figure 4-5 for further details. (Derived from Moyers and Duce.[349,350])

size. Similar results were obtained by Duce et al.[117] The major mass of bromide is found on particles with radii of 1-5 μm. Particulate bromide was also measured in Antarctica and ranged from about 1 ng/SCM at the coastal McMurdo site (about 300 km from open water) to about 0.5 ng/SCM at the South Pole, 2,800 m above sea level.[118]

Moyers and Duce[349] and Duce et al.[118] also measured the concentration of gaseous bromide in Hawaii and Antarctica. The chemical form of the gaseous bromide is unknown, like that of chloride. Concentrations found in these locations are given in Table 4-3. Near sea level in Hawaii, approximately 80-90% of the total bromide is in the gas phase, compared with about 35-40% of the total chloride. Moyers and Duce[349] point out that, over a reasonable pH range, simple thermodynamic considerations suggest oxidation of bromide to bromine by oxygen in the sea salt particles, and release of the bromine to the gas phase can explain the concentration of gaseous bromide found in marine air, whereas simple release of hydrogen bromide cannot. Photochemical reactions probably play an important role in the chemistry of gaseous bromine compounds.[527] Moyers and Duce[349] point out that the high bromide:chloride ratios in rain collected in Hawaii can be explained quantitatively by the dissolving of gaseous bromine or hydrogen bromide in the rain at the pH of rain found in that area (5-6). Previously, Seto et al.[420] had shown that the chloride:sodium ratio in rain collected in that area did not vary with respect to altitude or distance from the sea, indicating that the high bromide:chloride ratios in the rain are due to bromide gain, rather than chloride loss.

Duce et al.[117] and Moyers and Duce[350] suggested that the tendency for the bromide: chloride ratio to increase on the smaller particles could result from the collection of nonmarine particles containing bromide, perhaps

TABLE 4-3

Halogen-Compound Concentrations in the Natural Atmosphere

Location	Chloride, μg/SCM		Bromide, ng/SCM		Iodide, ng/SCM	
	Gaseous	Particulate	Gaseous	Particulate	Gaseous	Particulate
Hawaii, sea level[116,225,349,350]	2.7 ± 1.7	4.5 ± 1.3	46 ± 13	8.6 ± 2.8	8.1 ± 3.5	2.5 ± 0.9
McMurdo, Antarctica, sea level[118]		0.7 ± 0.08	7.9 ± 2.0	0.96 ± 0.37	2.2 ± 0.6	0.93 ± 0.39
South Pole, Antarctica, 2,800 m[118]		≤0.1	7.4 ± 2.6	0.43 ± 0.06	2.7 ± 0.8	0.49 ± 0.12

anthropogenic. This was also suggested by Cadle[62a] to explain the high bromide:chloride ratios found in stratospheric aerosols.

Moyers and Duce[349] calculated that gaseous bromide had a residence time approximately 7 times that of particulate bromide in marine air. With a particulate residence time similar to that of chloride, 2-4 days, this would result in a gaseous bromide residence time of 2-4 weeks.

Iodine. There has been considerable interest in the atmospheric chemistry of iodine in marine air for a number of years.[69, 104, 115, 116, 205, 280, 343, 499] Iodine appears to behave very differently from chlorine and bromine in marine air. Atmospheric particles and rain in marine air have iodide: chloride ratios ranging from 100 to 1,000 times the ratio in seawater, although the sea is almost certainly the source of both elements in uncontaminated air. The high ratios in the atmosphere are the result of either iodide enrichment on the sea salt particles when they are produced at the sea surface (perhaps owing to an association of iodide with surface-active organic material present on the sea surface) or iodide gas escape from the surface of the sea with later deposition on the surface of the particles.

Duce et al.[117] and Moyers and Duce[350] measured the iodide and chloride concentrations on different-sized particles in Hawaii with a cascade impactor for particle collection. The total particulate iodide concentration is approximately 2-3 ng/m^3. The variations in iodide and chloride concentrations and iodide:chloride ratio with particle size are shown in Figures 4-5 and 4-6.[350] Clearly, the maximal iodide concentration is on smaller particles than the maximal chloride concentration, resulting in an increase in the iodide: chloride ratio with decreasing size. Similar results were obtained by Duce et al.[117] Particulate iodide was also measured at antarctic stations,[118] and the concentrations are reported in Table 4-3.

Gaseous iodide was also measured by Moyers and Duce[350] and Duce *et al.*[118] in Hawaii and Antarctica and the concentrations found are reported in Table 4-3. Like those of bromide and chloride, the chemical form of gaseous iodide is unknown. Approximately 70-75% of the total iodide is in the gas phase near sea level.

Laboratory studies by Miyake and Tsunogai[343] and Martens and Hariss[323] with iodine-131 tracer have shown that gaseous iodine can be released from seawater by photochemical oxidation of iodide in the sea. Seto and Duce[419] questioned the validity of these experiments, inasmuch as nonradioactive gaseous iodine was removed from the air coming into the model system, thus upsetting any equilibrium between gaseous and aqueous iodine relative to ambient conditions. Moyers and Duce[350] point out that, at the concentrations of iodide and iodate present in seawater and iodine gas present in the atmosphere (assuming it is iodine), gaseous iodine should be dissolving in the sea, rather than released, if simple ionic thermodynamics apply.

Seto and Duce[419] show evidence that particles are enriched in iodide when they are formed at the sea surface and that the iodide is associated with organic material. They point out, however, that the enrichment of iodide found by this mechanism is only 10-20% of that found in ambient marine air, and they state that gaseous iodide is clearly a major factor in determining the iodide enrichment on particles. The mechanism for getting this additional gaseous iodide into the atmosphere is still unknown. Moyers and Duce[350] suggest, on the basis of thermodynamic considerations of iodide, iodate, and gaseous and aqueous iodine, that atmospheric sea salt particles should be a perfect sink for atmospheric iodine. Duce *et al.*[117] pointed out that the iodine:chlorine ratio on sea salt particles was inversely proportional to particl radius. This distribution would occur if the majority of iodine on the particles resulted from gaseous iodine diffusion to the particle surface. This idea was supported by Robbins.[396] Moyers and Duce[350] also point out, however, that the iodine:chlorine ratio variation with particle size parallels the atmospheric residence time of particles, as reported by Esmen and Corn.[135] They suggest that the increase in iodine on the particles may be controlled by the rate at which the thermodynamically stable species of iodine, iodate, is formed on the aqueous particles. Moyers and Duce[350] state that iodine is not the thermodynamically stable species in the gas phase. Reactions with both methane and hydrogen to form methyliodide and hydrogen iodide are thermodynamically favorable but kinetically very slow. Other organic species may also be present. Lovelock _et_ _al_.[309] have recently reported the presence of methyliodide over the ocean. They believe that this is the major form of gaseous iodine in marine air and that its source is the marine biomass. Photochemical reactions involving gaseous iodine species are probably very important but little work has been done on this subject.[527]

Quantitative estimates of the atmospheric residence time of gaseous and particulate iodine have not been made. Duce _et_ _al_.,[118] using measurements at coastal and inland antarctic stations, found that particulate and gaseous iodine both have longer residence times than the bromine species, which were 2-4 days and 2-4 weeks, respectively.

Fluorine. There have been very few studies of fluoride in the uncontaminated atmosphere. Carpenter[67] summarized the results of rain analyses for fluoride and pointed out that the fluoride:chloride ratios in rain samples, almost all of which were collected in continental areas, were 10-1,000 times the seawater ratio. Carpenter[67] and Sugawara[458] conclude that fluoride is preferentially (relative to chloride) injected into the atmosphere from the sea surface, thus explaining the high ratios.

However, Wilkniss and Bressan[515,516] have investigated the chemistry of fluoride and chloride in rain, as well as atmospheric particles in the field and in the laboratory. They do not report fluoride concentrations, but they find that, at midocean sites, away from the influence of land, the fluoride:chloride ratio in particles is near or a little below the seawater ratio, suggesting that chemical fractionation during sea salt particle production is not occurring to any important extent. This was supported by model studies in the laboratory. Atmospheric particulate samples collected over the ocean, but near the east coast of the United States, by Wilkniss and Bressan[516] showed fluoride:chloride ratios from 2 to 25 times the seawater ratio. The authors point out that these high ratios are most likely due to the incorporation of continental material into the marine aerosol that they were sampling. This is probably also the explanation for a large part of the high ratios found in precipitation. Wilkniss and Bressan also measured the ratio in the rain collected in Hawaii and found it equal to or less than the seawater ratio at altitudes up to about 500 m, but considerably higher at higher altitude. The reason for the increase is uncertain, but it is probably related to the fact that the mass of continental aerosols is greater than that of sea salt particles at higher altitude.

Wilkniss and Bressan[516] present laboratory evidence that gaseous fluoride is released from sea salt particles. The relation between gaseous fluoride and the high fluoride:chloride ratios in rain is not known. No attempt has been made to measure gaseous fluoride, except in the marine atmosphere, and the importance of sea salt particles as a source of gaseous fluoride has not been investigated. Carpenter[67] suggests that as much as 10^9 kg of fluoride per year, as hydrogen fluoride, may be released to the atmosphere from volcanoes. Lovelock[308] reports that about 10^9 kg of fluorine-containing compounds, such as the freons and sulfur hexafluoride, are released into the atmosphere each year. This is equivalent to about 2-4 x 10^8 kg of fluoride per year. Trichlorofluoromethane and sulfur hexafluoride have been measured in the atmosphere in a remote area of southwest Ireland by Lovelock.[308] Concentrations measured in westerly winds off the ocean were 0.01 ppb for trichlorofluoromethane and 0.029 ppt for sulfur hexafluoride. Concentrations were about 10 times greater with easterly winds off the European continent.

ATMOSPHERIC CHEMISTRY OF ANTHROPOGENIC CHLORINE COMPOUNDS

Sources of Urban Atmospheric Chlorides

Despite the possibility of significant amounts of chloride-containing material in urban atmospheres, very few measurements have been published. In urban air, chlorine-containing compounds can exist in gaseous form or combined with material in aerosols. Particulate chloride has been identified primarily with lead halides from motor-vehicle emission and with natural sodium chloride mixed with material of urban origin. The chloride associated with lead should be in submicrometer particles, but sea salt will influence heavily the composition of larger particles in cities to the leeward of oceans or influenced at times by influxes of marine air. Some typical particle size observations reviewed by Lee and Patterson[296] are shown in Figure 4-7. The data available suggest that the bulk of the particulate chloride will normally be found in the fraction larger than a few tenths of a micrometer in diameter. Comparison of Tables 4-2 and 4-4 suggests that the concentrations of *particulate* chloride in urban air are similar to those in the nonurban, marine atmosphere. However, the total urban and nonurban chloride concentrations are very different.

The gaseous compounds are believed to be principally hydrogen chloride and chlorine, although organohalides also have been observed including trichlorofluoromethane, methylene chloride, and DDT. Hydrogen chloride is

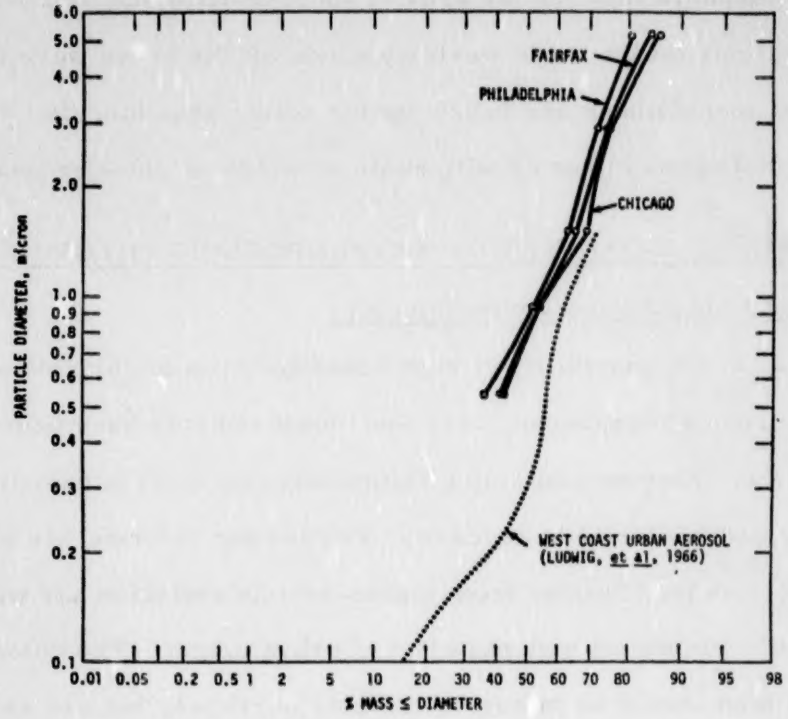

FIGURE 4-7. Cumulative particle size distributions of chloride in Chicago; Philadelphia; Fairfax, Ohio; and the West Coast. (Reprinted with permission from Lee and Patterson.[296])

thought to be more prevalent than chlorine, except near special isolated sources.

Ambient Concentrations in Urban Areas

Particles and Gases. Because the urban concentration of chloride generally has been found to be very low, compared with those of other pollutants, this material has not been studied in detail in cities in the United States. Interestingly, most of the estimates for gaseous chlorine species in city air must be derived from sources outside the United States.

Some total chloride concentrations are listed in Table 4-4. Particulate chloride concentrations are listed in Table 4-5. The gaseous chlorine species (as chloride) appear to dominate. The available information on ambient chloride in urban air is scarce and poorly documented, but the values listed suggest an upper limit of $\leq 100\ \mu g/m^3$ away from specific sources in American cities. This appears to be about 10 times or more larger than the concentrations in the middle-latitude nonurban air.

Pesticides. The extensive use of pesticides for agricultural purposes must be considered in the atmospheric chemistry of chlorine. Although most of the pesticides used are high-molecular-weight organohalides, there is some evidence of an unusually high volatility in the atmosphere at concentrations below the parts-per-billion range. For example, the widespread dispersal of DDT in the oceans cannot be explained readily by the fallout of large aerosol particles from insecticide sprays. More direct evidence of volatilization comes from laboratory experiments of Safe and Hutzinger.[407]

The halogen-containing pesticides should also be susceptible to photodecomposition in the atmosphere. Very little is known about such reactions under atmospheric conditions, but Hutzinger *et al.*[233] have speculated about reactions involving polychlorinated biphenyl compounds (PCB's).

TABLE 4-4

Concentration of Particulate Chloride in Urban Atmospheres

Location	Date	Concentration, $\mu g/m^3$	Reference
Los Angeles	1965	3	Ludwig *et al.*[310]
Pasadena	1969	0.10	P. K. Mueller *et al.* (in Miller *et al.*[341]
Chicago	1969	3.54	Lee and Patterson[296]
Philadelphia	1969	3.02	Lee and Patterson[296]
Fairfax, Ohio	1969	2.50	Lee and Patterson[296]
San Francisco	1970	2.93	John *et al.*[247]
Niles, Michigan	1971	<1.2	Rahn *et al.*[389]

TABLE 4-5

Concentration of Total Chloride in Urban Atmospheres

Location	Date	Concentration, μg/m³ Average	Range	Reference
Windsor, Ont.	1950	145	0 - 949	Katz[269]
Donora, Pa.	1949	109	0 - 459	Katz[268]
Cincinnati	1946-1951	50.4	0 - 291.0	
Charleston	1950-1951	24.5	0 - 104	
Baltimore	1950	56.6	1.5 - 168	
Niagara Falls, New York	1971-1973	85	0 - 570	Glotko[174]
Japan	1965	536	--	Seijo[417]
Berlin (near incinerator--1,500 m downwind)	1970	--	38 - 132	Lahmann and Moeller[288]
Japan	1967	--	10 - 23	Okita and Nakamura[365]
Japan, Tokushima Prefecture	1970	--	52 (maximum) <15 (generally)	Matsuoka *et al*.[327]
Japan, Tokyo - Chiba/Ichihara.	1969		91.8 - 150	Environmental Sanitation Center[245]
Germany (near potassium plant--2,000 m downwind)	1972	1,500 (without scrubbers)		Kirsch[275]
USSR	1961	150	--	Rjazanov[395]
Global	(estimated)		1 - 5	Junge[256]

Although the fate of airborne pesticides constitutes an important aspect of atmospheric pollution chemistry, chloride from these materials is generally found in concentrations of nanograms per cubic meter or less away from sources. Therefore, their contribution to the atmospheric chloride burden is considered negligible, compared with that of other sources.

Precipitation. Significant amounts of chloride have been found in rainwater samples. It was noted earlier that rainwater sampling indicated that chloride content generally decreases away from the seacoasts, except for cases of anomalously high concentrations in some cities. A comparison of chloride in rainwater between selected cities and nonurban areas is shown in Figures 4-2 and 4-3. The systematic surplus of chloride in rainwater in cities, particularly in the Midwest and East, suggests the influence of anthropogenic sources, presumably fuel combustion and industry.

Dispersion of Chlorine Compounds in the Atmosphere

There are no known anomalies in the dispersion of chlorine compounds in the atmosphere. Thus, the material from anthropogenic or natural sources is expected to be transported and mixed by air motion in essentially the same manner as other trace contaminants. The dispersion of contaminants in the atmosphere has been a subject of extensive investigation for many years. The general methods for estimating mixing rates and transport have been reviewed by several investigators (e.g., Wanta[504]).

General transport and dispersion are common to all materials emitted into the atmosphere, and a variety of information is available elsewhere; these subjects will not be treated further here. It should be pointed out, however, that chlorine gas is denser than air. Under very stable atmospheric conditions with light winds, chlorine compounds tend to concentrate near the ground.

Transformation Process

Chlorine compounds can react chemically in the atmosphere to be transformed into several classes of materials, including oxidized species. The atmospheric reactions of gaseous chlorine compounds have been studied to an appreciable extent only in the recent years. It is anticipated that photochemical reactions that produce atomic chlorine will be of greatest interest, because they may play a role in the behavior of atmospheric ozone. Several reactions of potential importance can be written, as follows:

$RCl + h\nu\ (185 < \lambda < 220\ nm) \rightarrow R + Cl$		
$Cl_2 + h\nu\ (\lambda \leq 475\ nm) \rightarrow Cl + Cl$		(Reaction is very rapid, owing to the high intensity of visible light)
$Cl + O_2 + M \rightleftarrows ClOO + M$	(1)	
$Cl + O_3 \rightarrow ClO + O_2$	(1)	(This pair of reactions constitute the primary mechanism proposed for the destruction of ozone in the stratosphere)
$ClO + O \rightarrow Cl + O_2$	(1)	
$Cl + H_2 \rightarrow HCl + H$	(1)	(Main reactions forming HCl, which serves as a chlorine reservoir)
$Cl + CH_4 \rightarrow HCl + CH_3$	(1)	
$Cl + CO + M \rightleftarrows ClCO + M$	(2)	
$ClO + CO \rightarrow CO_2 + Cl$		
$Cl + HO_2 \rightarrow HCl + O_2$		(Data are needed on this reaction)
$Cl + OH \rightarrow HCl + O$		(Atmospheric concentration of OH is low)
$ClO + O_3 \rightarrow ClO_2 + O_2$	(1)	(Reaction is very slow)
$ClO + NO \rightarrow NO_2 + cl$	(1)	(Competes with $ClO + O \rightarrow Cl + O_2$)
$ClO + ClO \rightarrow ClO_2 + Cl$	(1)	(Atmospheric concentration of ClO is low)
$HCl + OH \rightarrow H_2O + Cl$	(1)	(Important step for regenerating Cl atoms in stratosphere)

The possible mechanisms for chlorine catalysis in the stratosphere following photolysis of a chlorine compound have been reviewed in detail by Watson [505b] and by Rowland and Molina [405a]. Their potential importance to air pollution appears to have been recognized a few years ago by Johnston. [248] Reaction rates have been reported for the systems cited with numbers in parentheses -- (1) Hampson and Garvin[188a] (2) Burns and Dainton [60].

It is possible that many reactions would be important in both the troposphere and the stratosphere if gas-phase chlorine compounds were ever to reach significant concentrations. What constitutes a significant concentration would be a function of the light intensity, the total atmospheric pressure, and the abundance of radical scavenging material, such as particulate matter.

The most significant reactions of chlorine compounds in the atmosphere would occur after the photochemical dissociation of gas-phase hydrogen chloride, chlorine, or other chlorinated compounds to produce free chlorine atoms. Molecular chlorine is rapidly photolyzed by visible solar radiation. It can be considered as a steady source of Cl atoms. Gaseous hydrogen chloride, requiring higher energy for dissociation, would be expected to be of photochemical significance only at higher altitudes, where there is an abundance of low-wavelength radiation. However, even in the stratosphere photolysis is less important than the reaction of HCl with OH.

Once the chlorine atoms have been produced, they will proceed to catalyze chain reactions and produce other reactive free-radical species, until they are removed from the atmosphere. The removal processes consist only of radical-radical recombination reactions and scavenging by particulate matter or water droplets.

The low concentration of radical species in the troposphere makes the recombination reactions very slow, so the major termination reactions would be expected to occur on particle surfaces. At higher altitudes, where the radical population would be greater, the recombination reactions should be of greater significance. However, even for the stratosphere these recombination reactions are believed to be relatively unimportant.

In either case, the free radicals would be expected to react mainly with molecular species in which a free-radical species would always be generated as one of the products.

Many of the chlorine chain reactions rely on the production of the ClO free radical. The principal formation reaction is $Cl + O_3 \rightarrow ClO + O_2$ (in the stratosphere). Other, speculative, possible reactions are included in the foregoing list. Free-radical reactions of these types can also occur with hydrocarbons or water, producing other free radicals, such as OH, HOO, RO, and ROO, all of which will have many reactions of their own. Hence, the importance of the role of chlorine as a sensitizing agent in the atmosphere is limited only by its concentration and the presence of radical scavengers that terminate the free-radical production chains.

In the lower atmosphere, the principal reactions of hydrogen chloride are assumed to be physical and probably involve water or aerosols.

Recently, considerable concern has been expressed about the increasing ambient concentrations or organochlorine compounds, particularly the chlorofluoromethanes("Freons"). An extensive review of the problem is given by Rowland and Molina [405a]. The chlorofluoromethanes, e.g., CCl_2F_2 and CCl_3F, and similar materials, such as carbon tetrachloride and methyl chloride, are believed to be stable in the troposphere, without major removal paths. After diffusion into the stratosphere, they may dissociate in ultraviolet radiation to form chlorine atoms which can undergo catalytic reactions with stratospheric ozone. Such predictions have raised concern about anthropogenic organohalogen compounds emitted at the ground. The NAS/NRC Climatic Impact Committee's Panel on Atmospheric Chemistry, chaired by Dr. H. S. Gutowsky, will report later on the effects on stratospheric pollutants on the ozone layer.

Tropospheric Processes in Urban Atmosphere

Sodium chloride and presumably other halogen-containing salts undergo attack by acid-forming gases to release hydrogen chloride gas (see eqs. 5 and 6). There is considerable circumstantial evidence of this effect from measurements of the chloride:sodium ratio in West Coast cities. In urban areas, where relatively high concentrations of nitrogen dioxide may be present, the chloride:sodium ratio is much lower than would be expected from sea salt if it were reduced by addition of soil dust to the aerosol.

Pierrard [381] discussed the implications for atmospheric chemistry of the photodecomposition of lead halides from auto exhaust. Experimental observations suggested that the rate of release of chlorine from lead bromochloride, for example, would be $0.8\text{-}1.3\times10^{-6}$ micromole/cm^2-sec per milliwatt per square centimeter of sunlight.

For conditions of heavy freeway traffic, where lead bromochloride concentrations can be as high as 30 $\mu g/m^3$, Pierrard calculated that the photochemical release of chloride from such aerosols would be about 0.1 ppb/hr. For the residence time of air masses of about 1 day in Los Angeles, for example, this release would give a negligible amount of chlorine atoms in polluted air. Robbins and Snitz [397] have measured the loss of chloride from lead halides in air and have found that the chloride is volatilized independently of sunlight. The loss rate of chloride observed by these investigators was exponential in the chloride:lead ratio, with the time constant of 0.003 ± 0.002 per minute.

ATMOSPHERIC REMOVAL PROCESSES

Although chlorine may be present initially in gaseous and particulate form, the transformations that its compounds undergo will not remove chlorine from the atmosphere. The removal processes are uncertain. However, the role of aerosols and rain are identified as potentially significant. Gaseous chloride may also be absorbed at the earth's surface either by the oceans or by soil. The path of removal of chloride is probably through aerosols and by water cloud processes. These processes have been described for other reactive trace gases by Hidy[208].

Particles

It is difficult to determine the relative importance of dry fallout or impaction and precipitation for the removal of chloride from uncontaminated air. In his studies of the global sea salt budget, Blanchard[42] estimates that, for wind speeds of 12 knots in Hawaii, the average salt removal from the atmosphere by fallout is 5.1×10^{-6} μg/cm^2-sec, corresponding to 3.1×10^{-6} μg of chloride per square centimeter per second. The calculated value for rainfall removal of chlorine under the same conditions is 5.8×10^{-6} μg/cm^2-sec. Thus, approximately 35% of the salt is removed by dry fallout, and 65% by precipitation (assuming that all the chloride in the rain comes from the particles). In Eriksson's[133] study of the global sea salt budget, he makes calculations based on river runoff and rainfall chloride concentration in Scandinavia. He estimates that approximately 50% is removed by dry fallout, and 50% by rain. Silker,[432] using measurements of beryllium-7, suggests that rainfall is the primary mechanism for aerosol removal over large areas of the tropical oceans. From these estimates, it appears that perhaps 50-75% of the particulate chloride is removed by rainfall, and 25-50% by dry fallout.

The residence time of atmospheric sea salt particles depends, of course, on particle size. Junge[257] and Eriksson[133] made estimates of the residence time of sea salt particles over the ocean. These are presented in Table 4-6. For the major mass of atmospheric chloride, with particle radius of 1-3 μm (at 90% relative humidity), the residence time is apparently about 1-4 days.

Gases

The gaseous chloride species in the atmosphere must be removed by rainfall, adsorption on particles, or direct uptake by the earth's surface. Data on this subject are almost completely lacking. Duce[114] has pointed out that, for

TABLE 4-6

Calculated Residence Times of Sea Salt Particles over the Ocean

	Sea Salt Particle Mass, g			
	10^{-12}	10^{-11}	10^{-10}	10^{-9}
Particle radius, μm (90% R.H.)	1.3	2.6	5.5	11
Residence time, days:				
Eriksson[133]	3.5	1.0	0.6	0.5
Junge[257]	1.9	1.6	1.0	0.3

rainwater in marine air in Hawaii with a pH of 5-5.5 and a chloride concentration of 1 mg/liter (or $10^{-4.5}$ M), the pressure of hydrogen chloride in equilibrium, according to Eq. 4, should be about 10^{-16} atm, one ten-millionth of the partial pressure of gaseous chloride actually observed, assuming that it is hydrogen chloride. Thus, hydrogen chloride should dissolve in rain readily. However, Duce et al.[114] showed that the chloride:sodium ratio did not vary with rainfall intensity or raindrop size and suggested that the exchange of gaseous and dissolved chloride was a minor factor in the variation in chloride concentration in the rain. This again supports the suggestion that gaseous chloride has a longer residence time than particulate chloride over the ocean. The small variation in gaseous chlorine compounds during rain in Hawaii found by Junge[255] and the fact that chloride:sodium ratios in rain are generally below the seawater ratio of 1.80:1 also suggest that precipitation may not be a very rapid removal mechanism for gaseous chlorine species.

Gaseous pollutants are also known to be exchanged with vegetation. Hill,[212] for example, has reported experiments on the rate of absorption of chlorine by alfalfa. His studies indicate that, the more water-soluble a gas, the higher the uptake in plants. Wind speed and light intensity were noted to influence absorption. The rate of uptake of chlorine increased with increasing gas concentration in air over a range. At higher concentrations of this pollutant, the absorption was partially limited by closure of stomata.

The extent to which gaseous chlorine compounds adsorb on the surface of atmospheric particles other than sea salt is unknown. The surface of the ocean, with a pH of 8.3, may be a significant sink for gaseous hydrogen chloride, but there are no experimental data available to support this. The land surfaces, vegetation, alkaline soils, etc., are also undoubtedly efficient sinks, but again there is no quantitative information available. This is clearly a subject for future research.

From the very limited data available, it is difficult to estimate a residence time for gaseous chloride in the uncontaminated marine atmosphere, but it is instructive to see what ranges of values can be obtained. We will make the simplifying assumption that naturally occurring gaseous chloride is essentially absent over the continents. We will assume from the meager data in Table 4-2 that the average gaseous chloride concentration over the ocean is 3 μg/SCM from sea level to 700 mb, 1.5 μg/SCM from 700 to 400 mb, and 0.75 μg/SCM above 400 mb. With an atmospheric volume over the oceans of about 2.9×10^{18} SCM, this results in 4.7×10^{9} kg of gaseous chloride present in the marine atmosphere at any time. Combining this value with the previously estimated gaseous chloride production rate of about 100-900 $\times 10^{9}$ kg/year results in a gaseous chloride residence time range of 2-17 days. This range could be increased by up to 25%, if some of the gaseous chloride produced in the marine atmosphere is found over the continents, as it certainly is. Although these numbers must be considered as very tentative, they are, at least, in a reasonable range.

INADVERTENT WEATHER MODIFICATION

There is ambiguous evidence that some atmospheric pollutants, such as carbon dioxide and aerosols, have a measurable influence on the radiative transfer of heat in the atmosphere or on the perturbation of cloud formation. Thus, there may be concern that the chloride-containing pollutants would reach concentrations that could influence the earth's weather. Because of the low concentration of chloride gases in the ambient air, it is unlikely that such material would strongly influence the radiative transfer processes in the lower atmosphere. However, the tendency for hydrogen chloride and chlorine to dissociate with light absorption may make them of potential importance in the ozone cycle. This may be of concern, particularly in the upper atmosphere, in the use of large rocket boosters in the space-shuttle program, in which rocket engines emit locally significant quantities of hydrogen chloride and chlorine.

Chloride in airborne particles might be a disturbing influence in the nucleation of water droplets or ice in clouds. It is well known that sea salt or other hygroscopic particles larger than 0.1 μm in diameter are good cloud condensation nuclei. Soluble chloride particles found in an urban environment might add active condensation nuclei to the nonurban background. The low mass concentrations of particulate chloride combined with the possibility of removal of chloride by acid-gas reactions on particles appears to weaken the potential influence of chloride with respect to condensation nuclei. Schaefer[412] has speculated that lead halides, especially lead iodide, will make a significant change in ice nuclei concentrations downstream from cities. Lead iodide has been used as a nucleation or cloud seeding agent in a manner similar to that of silver iodide.[155] However, some crude measurements of ice nuclei taken upstream from Los Angeles and in Los Angeles, as reported by Hidy et al.,[210] did not provide any evidence of this kind of disturbance.

There appears to be no evidence of any influence of anthropogenic chlorides on weather.

CHAPTER 5

EFFECTS OF CHLORINE AND HYDROGEN CHLORIDE ON MAN AND ANIMALS

The natural history of a disease (including intoxication) tends to become evident at first through the most advanced cases. It is ordinarily only then that the early, more limited, subtle characteristics of the problem are recognized. These prodromal characteristics may or may not be similar to the more obvious ones. With chemical exposures, this can happen for a variety of reasons: dose, duration of exposure, threshold of response, interspecies and intraspecies variability, etc.

In many cases, the responses of a biologic system to chemical exposures appear to depend on both the dose and the duration of exposure. Observations of effects of acute exposures to high concentrations of a chemical may contribute little to the understanding of the effects noted at the other end of the scale. Chronic exposure to low concentrations of hydrogen chloride is a case in point. Acute high-concentration exposures produce irritation of the respiratory tract;[322] chronic low-concentration exposures apparently produce no respiratory problems, but cause erosion of the teeth.[469,481]

PHYSICAL STATES OF CHLORINE AND ROUTES OF EXPOSURE

Chlorine, regardless of its divergent sources and variety of uses, is found in only two states: gas and liquid.

Although liquid chlorine can cause eye and skin burns, the most common state of chlorine in adverse exposures is the gaseous state. Therefore, the most important route of exposure is inhalation. Less significant routes of exposure to the gaseous state are ocular and cutaneous.

MECHANISMS OF ACTION OF CHLORINE

Chlorine is a most reactive element and readily combines with a variety of organic compounds and radicals well justifying its reputation of a general protoplasmic poison. Its reactivity is epitomized by the readiness with which it displaces other halogens, bromine and iodine in particular, from their salts.[295]

Chlorine persists as an element only at very low pH (less than 2); in less acid solutions (such as living tissues), it rapidly converts to hypochlorous acid (HOCl).[529] Hypochlorous acid apparently penetrates the cell wall easily, promptly reacting with cytoplasmic proteins to form N-chloro derivatives that destroy the cell structure.[295] Although the toxic sequence of the process is not clearly established, cell-wall damage is one of the most immediate effects of chlorine. Radioactive-tracer studies by Friberg have demonstrated that small amounts of chlorine are effective in disrupting bacterial wall permeability, which leads to leakage of the marker into the watery medium.[152] This cell-wall lesion explains the acute effects of chlorine: its edematogenic effect and its corrosive injury of exposed surfaces. The biochemical correlates of this injury have been studied almost exclusively in microbiologic models.

The inhibition of carbohydrate metabolism was originally suggested on the basis of the decreased glucose oxidation observed in bacteria treated with a dilute chlorine solution.[182] The reactivity between sulfhydryl groups and chlorine and the evidence of inhibition of sulfhydryl-dependent enzymes have suggested this as the most likely site for the action of chlorine.[279] This hypothesis has been challenged. Experiments with viruses suggest that compounds active toward sulfhydryl groups are not always virucidal.[6,84] Inactivation of RNA appears important in chlorine toxicity, as documented in recent observations of virucidal effects.[367]

Lethal effects on elementary forms of life (bacteria, fungi, etc.) exposed to chlorine in water occur at about 1 ppm (range, 0.05-5.0 ppm) with contact duration of a few seconds (range, 1-120 sec). However, some bacteria (such as Mycobacterium tuberculosis) and some fungi (such as Aspergillus niger) require much higher concentrations--in excess of 50 ppm.[295]

Oxidation has been traditionally considered an important step in the germicidal action manifested by hypochlorous acid and other halogenated species. This mechanism was proposed some 70 years ago[404] as the basis of cellular necrosis and bactericidal effect. However, as clearly outlined by Morris,[346] the temptation to formulate mechanism of bactericidal action on the basis of oxidation potential is not justified. Hydrogen peroxide, for instance, with a strong oxidation potential, has very limited bactericidal strength. Analysis by electron-spin resonance spectroscopy of radicals associated with oxidation does not indicate the presence of atomic oxygen.[160] In fact, the nature and importance of the reactivity or presence of "activated" oxygen often mentioned in the old literature remains unsubstantiated, in the opinion of a recent reviewer.[197]

EFFECTS OF CHLORINE ON NONMAMMALIAN SPECIES

Chlorine is used to treat public drinking water supplies and the water supplies and effluent of sewage treatment plants, textile mills, power plants, and various other industries. Some industries chlorinate continuously; in others, in which chlorination is used to control marine fouling, the practice is to "slug" with high concentrations for short periods. Chlorine added to water containing nitrogenous materials rapidly forms chloramines. The ultimate toxicity to various forms of acquatic life depends on the concentrations of chlorine and chloramines and on species variability. In the life cycle of the fathead minnow, for example, egg production reportedly is the link most sensitive to chlorine. [305, 336, 358, 529]

Aside from aquatic animals, it has been reported that chronic ingestion of chlorinated water produces vascular changes in chickens.[386]

EFFECTS OF CHLORINE ON MAMMALIAN SPECIES OTHER THAN MAN

Lethality of Single Inhalation Exposures to High Concentrations

The toxicity of inhaled chlorine varies greatly in different reports. The variability might be related to type, size, or shape of exposure chambers, to completeness of mixing of chamber atmosphere, to mode of operation (whether static or dynamic), to variations in gas absorption in chamber or animals, to method of determination of concentration of airborne chlorine, to species, to concentration, to exposure time, etc. Underhill compared the experimental results on dogs and found them consistent when dogs were exposed individually, but inconsistent when they were exposed in pairs.[487]

There is also confusion in the terms used in the literature to describe the airborne toxic dose. Haber introduced the concept of mortality product or lethal index (the Haber product of mortality):[384] the product of the concentration of gas inhaled (in milligrams per cubic meter) and the exposure time (in minutes) that will kill animals. This product, as considered by Flury and cited by Sartori, was considered to be the minimal lethal value.[410] After the advent of statistical treatment of data, the term LCt_{50} was introduced. Ct is a measure of airborne dose or total exposure: C refers to concentration (in milligrams per cubic meter), and t refers to time (in minutes). The product Ct is expressed in milligram-minutes per cubic meter ($mg\text{-}min/m^3$). The term LCt_{50} indicates the dose (Ct) that is lethal (L) to 50% of an exposed population.

There are some weaknesses in the use of Ct. There is no provision for differences in breathing rates between individuals. However, this difference seems to lose importance when groups of animals are compared. For a given substance, Ct values developed with low concentrations and long exposure times are greater than those developed with high concentrations and short exposure times. The former situation affords a better opportunity for detoxification.

In reporting Ct values, the exposure time should be mentioned. Despite these weaknesses, Ct values do provide a convenient and useful measurement of total exposure or airborne dose.

The general results indicate that there is much species variation in the toxicity of chlorine. Mice are more susceptible than dogs, and (although this is less adequately documented) cats seem more susceptible than mice.[410]

Information on lethality of chlorine in animals appeared in the literature as early as 1887.[148 (p. 119)]

Exposure to chlorine at 900 mg/m^3 (300 ppm) for 1 hr may kill cats, rabbits, and guinea pigs by asphyxiation.[136] Dogs rarely die after a 30-min exposure to concentrations less than 1,900 mg/m^3 (650 ppm) and never after a 30-min exposure at less than 800 mg/m^3 (280 ppm).[148] Brief exposure to air containing chlorine at 3,000 mg/m^3 (1,000 ppm) kills horses.[148]

Weedon et al.[508] exposed mice, rats, and houseflies to chlorine at 2,900, 725, and 183 mg/m^3 (1,000, 250, and 63 ppm). They also exposed the flies to 47 mg/m^3 (16 ppm). The animals were exposed for 16 hr or until death. It is known that deaths occur after, as well as during, exposure to chlorine. Thus, it is likely that many of the animals had received lethal doses at some time before death occurred.

The animals exposed at 2,900 mg/m^3 showed little early excitement. There was dyspnea, lacrimation, and foaming secretion of the nostrils. One mouse died in 21 min, and all were dead by 50 min. At 725 mg/m^3, the mice showed lacrimation during the first hour, and then dyspnea, terminal prostration, and convulsion. All the mice were dead in 8.4 hr. The first rat died in 6.4 hr, and all died by the sixteenth hour. At 183 mg/m^3, there were fewer effects and no deaths. Animals that died or were sacrificed for gross autopsy immediately after exposure showed distention, with foaming, hemorrhagic fluid in the lungs, and some congestion of the liver at all chlorine concentrations. Weedon et al.[508] gave the $Lt_{50's}$ that are shown in Table 5-1.

TABLE 5-1

$Lt_{50's}$ for Chlorine Exposures of Various Species[a]

	Lt_{50}, min			
	Chlorine concentration, mg/m^3			
	2,900	725	183	47
Animals				
Houseflies	45	240	840	>>960
Mice	28	440	>960	—
Rats	53	440	>960	—

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[a] Data from Weedon et al.[508]

Weedon et al. produced time-mortality regression lines by plotting their data on log-probit paper. The size of their published graphs made accurate reading of the values somewhat difficult. Several values from each graph were used to compute new lines by the Bliss method. Computed times to death for various percentages of the populations are shown in Table 5-2, and the values in Table 5-2 were used to calculate the LCt_{50} values shown in Table 5-3.

Silver and McGrath[433] exposed two strains of mice to chlorine for 10 min and found $LCt_{50's}$ of 15,200 ± 1,900 mg-min/m^3 and 17,300 ± 2,400 mg-min/m^3. The lowest concentration, 730 mg/m^3, killed two of 20 animals. Values derived from their graphs are shown in Table 5-4.

TABLE 5-2

Lt's for Various Percentages of Population Exposed to Chlorine[a]

Fraction killed, %	Lt, min				
	Chlorine concentration, 2,900 mg/m^3			Chlorine concentration, 725 mg/m^3	
	Houseflies	Mice	Rats	Mice	Rats
1	--	12	14	261	207
16	--	19	28	364	327
30	--	23	36	409	384
50	45	28	48	467	460
84	--	41	78	598	648
99	--	67	155	834	1,024

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[a] Computed from regression lines of Weedon *et al*.[508] The recalculation allows direct comparison with other values given in this chapter.[158, 433, 434]

TABLE 5-3

LCt's for Chlorine Exposures of Mice and Rats[a]

Fraction killed, %	LCt, mg-min/m^3			
	Chlorine concentration, 2,900 mg/m^3		Chlorine concentration 725 mg/m^3	
	Mice	Rats	Mice	Rats
1	34,800	40,600	189,225	150,075
16	55,100	81,200	263,900	237,075
30	66,700	104,400	296,525	278,400
50	81,200	139,200	338,575	333,500
84	118,900	226,200	433,550	469,800
99	194,300	449,500	604,650	742,400

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[a] Calculated from data of Weedon *et al*.[508]

TABLE 5-4

Dose-Response Regression Data for Lethality in Mice Exposed to Chlorine for 10 Minutes[a]

	Dose-Response Regression Data			
	Miscellaneous Mice		Selected Mice	
Fraction killed %	Chlorine Concen. mg/m^3	LCt, mg-min/m^3	Chlorine Concen. mg/m^3	LCt, mg-min/m^3
1	600	6,000	--	--
16	1,120	11,200	1,360	13,600
30	1,310	13,100	1,530	15,300
50	1,520	15,200	1,730	17,300
84	1,900	19,000	2,100	21,000
99	2,430	24,300	--	--

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[a] Derived from Silver and McGrath.[433]

In another investigation, Silver *et al*.[434] found an LCt$_{50}$ of 19,600 ± 1,900 mg-min/m^3 for a third strain of mice exposed to chlorine for 10 min. Deaths occurred at all concentrations. The lowest concentration to cause death was 1,100 mg/m^3. Most of the deaths were due to pulmonary edema. Some deaths occurred in the presence of slight edema accompanied by congestion, and deaths of a third type seemed to be related to secondary pneumonia. LCt's are shown in Table 5-5. The derived LCt's from Weedon *et al*.[508] for mice are much higher than those of Silver et al.[433,434] The former recorded deaths as they occurred during exposure, but Silver *et al*. included deaths that occurred after exposure. Shortly after exposure, the mice pawed at their noses and mouths. Labored breathing, gasping, yawning, and spasmodic contraction of the intercostal muscles began soon thereafter. The mice convulsed shortly before death. During a 10-day observation period after a given dosage, the number of deaths

TABLE 5-5

Dose-Response Regression Data for Lethality in Mice Exposed to Chlorine for 10 Minutes[a]

Fraction Killed, %	Dose-Response Regression Data Chlorine Concentration, mg/m^3	LCt, mg-min/m^3
1	970	9,700
16	1,550	15,500
30	1,750	17,500
50	1,960	19,600
84	2,500	25,000
99	3,300	33,000

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[a] Derived from Silver et al.[434]

per day was roughly constant. There were no pathologic findings in survivors 10 days after exposure.[434]

In mice exposed for 30 min by Schlagbauer et al., the LC_{50} dose (with 95% confidence limits) was 381 (range, 318-456) mg/m^3, or 127 (range, 106-152) ppm, for a 4-day observation period.[414] The LCt_{50} was 11,430 (range, 9,540-13,680) mg-min/m^3. In exposures of 3 or 6 hr at 10, 22, or 40 ppm, deaths occurred as a result of bronchospasm or pulmonary edema. Concentrations of 2.5-10 ppm for 8 hr/day for 3 successive days were not lethal. This was a Ct of 13,920 mg-min/m^3 for 1 day (29 mg/m^3 x 480 min) or 41,760 mg-min/m^3 for 3 days.

In dogs, deaths occurring in the first 3 days (most died within 24 hr) are due to immediate effects of the chlorine gas.[486] In animals that survive beyond the 3 days, the pulmonary edema subsides, and the animals later die of bronchopneumonia or recover. Table 5-6 shows some results of exposure of dogs to chlorine for 30 min, and Table 5-7 is a Bliss calculation based on these data.

Table 5-8 summarizes information on the lethality of chlorine in various animals.

Toxicologic Effects of Single Lethal or Near-Lethal Exposures

Studies in animals have generally confirmed and expanded the knowledge obtained from human exposure to chlorine during World War I. Immediately on exposure there is bronchoconstriction and a reflex slowing of respiration. The bradypnea is followed by tachypnea. Pulmonary edema, which develops rapidly, is followed by plasma loss and hemoconcentration. Anoxemia, acidosis, and cyanosis appear. Body temperature is increased by small doses of chlorine and decreased by moderate or high doses. As death approaches, the pulse rate increases and blood pressure decreases to the point of shock. This section summarizes briefly the experimental basis of what is known about the effects of chlorine.

Sudden Death. Sudden death without pulmonary lesions in man during WWI has been attributed to reflex action by Vedder[498] and to "respiratory paralysis" by Gilchrist.[166] In studies with unanesthetized and anesthetized (with ether) dogs and cats, the inhalation of pure chlorine produced a long expiration, respiratory arrest for 20 sec or more, and then slower-than-normal breathing. These changes in respiratory rhythm were abolished by cutting the vagi.[430,431] Intratracheal injection of pure chlorine produced cardiac arrest in anesthetized dogs and cats. Section of the vagi before injection prevented cardiac arrest.[430]

TABLE 5-6

Acute Deaths (within 72 Hours) in Dogs Exposed to Chlorine for 30 Minutes[a]

Chlorine Concentration, mg/m^3			
Median	Range	Median Ct, mg-min/m^3	Fraction killed within 72 hr, %
408	16- 800	12,240	0
1,425	1,270-1,580	42,750	6
1,740	1,580-1,900	52,200	20
2,060	1,900-2,220	61,800	43
2,375	2,220-2,530	71,250	50
2,690	2,530-2,850	80,700	87
4,645	2,850-6,340	139,350	92

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[a] Derived from Underhill.[486,487]

TABLE 5-7

LCt's for Chlorine Exposures of Dogs[a]

Fraction Killed, %	LCt, mg-min/m^3	95% Confidence Limits, mg-min/m^3
1	30,562	21,418-43,611
16	47,678	40,122-56,657
30	55,781	49,455-62,916
50	66,455	60,428-73,084
84	96,628	77,395-110,860
99	144,501	100,441-207,889

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[a] Derived from Underhill.[486,487]

TABLE 5-8

Lethality of Single-Inhalation Exposures of Animals to Chlorine

Animals	Chlorine Concentration, mg/m^3	Exposure Time, min	Ct, mg-min/m^3	Toxicity Value
Mice	1,800	10	18,000	LCt$_{50}$[158]
	1,520	10	15,200	LCt$_{50}$[433]
	1,730	10	17,300	LCt$_{50}$[433]
	1,960	10	19,600	LCt$_{50}$[434]
	1,820	--	18,200	LCt$_{50}$[434]
	2,900	28	81,200	LCt$_{50}$[508a]
	725	467	338,575	LCt$_{50}$[508a]
Rats	2,900	48	139,200	LCt$_{50}$[508a]
	725	460	333,500	LCt$_{50}$[508a]
Cats	--	--	7,520	Mortality product[127b]
Dogs	2,220-2,530	30	66,455	LCt$_{50}$[486,487c]
	2,500	30	75,000	Mortality product[16]
Not stated	3,000	30	90,000	Mortality product[498d]
Most animals	2,900	Few	--	Lethal for most[242e]
Most animals	40,000-60,000	30-60	--	Serious or fatal[242e]
Not stated	5,600	10	56,000	Mortality product[502d]
Not stated	5,600	10	56,000	Mortality product[384d]

TABLE 5-8 - Continued

Animals	Chlorine Concentration, mg/m^3	Exposure Time, min	Ct, mg-min/m^3	Toxicity Value
Not stated	2,530	30	75,900	Mortality product[384d]
Not stated[e]	50	30	1,500	Toxic[148,500f]
Not stated[e]	100	30	3,000	Fatal[148]

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[a] All exposures until death; LCt_{50} calculated from Ct at time when 50% of animals had died during exposure.

[b] "Mortality product" means "lethal Ct" or "minimal lethal Ct."

[c] Determined by Bliss method.

[d] No data or references to support toxicity values.

[e] No data. Reference is made to Sayers et al.[410a] Ind. Eng. Chem. 26:1251, 1934; Haggard,[184a] J. Ind. Hyg. 6:397, 1923-24; and Berghoff.[32]

[f] Wachtel[500] quotes Flury and Zernik,[148] who quote Lehman-Hes; fatal values given for man; basis for values not given.

Mayer et al.[330] noted that irritant vapors in the upper respiratory tract decreased or arrested respiration and circulation in rabbits and dogs. In some animals, the respiratory arrest was fatal. Irritant vapors that were inhaled deeply or through a tracheal cannula, so that they penetrated into the bronchi and lungs, produced an acceleration of respiration. The two reflexes were antagonistic. Simultaneous acceleration of the upper and lower respiratory tract caused the respiratory rhythm to be disorganized, spasmodic, and convulsive. The reflex causing the polypnea does not occur if the vagus nerve has been cut before inhalation. Tachypnea that had begun was abolished by section of the vagus nerve.

Bronchoconstriction. Gunn[184] found that the respiratory excursion of the lungs of anesthetized rabbits subjected to artificial respiration at constant pressure was reduced for about 1 min when chlorine was breathed. Gilpin,[171] in a similar experiment with decerebrate rabbits, found that chlorine caused an immediate spasm. Bronchospasm in pithed cats subjected to artificial respiration was relieved by stramonium fumes.[179] The intravenous administration of atropine was believed to have an antispasmodic action in unanesthetized rabbits that had been exposed to chlorine.[90]

Effects on Ciliary Activity. In 1915, Hill[213] reported that chlorine in water at 1:300 stops the movement of cilia. Schultz[431] found that the cilia of the tracheal mucosa were paralyzed after pure chlorine was introduced into the trachea; it is assumed that the animals used were unanesthetized dogs or cats. Cralley noted that irreversible cessation of the mucociliary activity of sections of excised rabbit trachea occurred at exposures to 30 ppm for 5 min. and 18-20 ppm for 10 min.[93] However, reversible ciliostasis was noted after exposure at 200 ppm for less than a minute and 20 ppm for 2.5 min.

Respiratory Rate, Pulse Rate, and Edema Formation. Underhill[487] exposed 112 dogs to chlorine at 160-6,340 mg/m^3 for 30 min. Inhalation of high concentrations of chlorine caused immediate respiratory arrest and bronchoconstriction. The average respiratory rate increased from 20 per minute to about 35 per minute during the first hour after exposure. It gradually subsided to about 25 per minute 13 hr after exposure. The pulse rate declined slightly during the first 4 hr after exposure followed by a rapid increase to double the normal rate at 10 hr. This pulse rate was maintained for 24 hr. These respiratory and cardiac changes corresponded to the development of pulmonary edema, which was measured in dogs sacrificed periodically beginning 30 min after 30-min exposure.[486] The edema develops rapidly; it was noted at the first sacrifice, which occurred 30 min after a dog had inhaled a concentration of 2,590 mg/m^3 for 30 min. Edema was present up to the last sacrifice, 312 hr after exposures of animals to chlorine at 1,450-2,930 mg/m^3.

Other investigators have reported on the effect of chlorine on respiration, pulse rate, and blood pressure. Concentrations of 29,000 mg/m^3 and 58,000 mg/m^3 initially caused a gradual, slight increase in blood pressure, with little change in respiration, in rabbits anesthetized by chloroform.[413] After 4 min, respiration became slower and deeper. The heart rate was slower, but blood pressure was maintained. At 5½ min, respiration suddenly became convulsive, and blood pressure, irregular. At 6½ min, respiration and blood pressure failed suddenly. The heart continued to beat for several minutes. Artificial respiration was ineffective when given 2½ min after respiration ceased.

The respiratory rate of rabbits anesthetized by a chloroform-ether mixture or ether alone increased during exposure to 580-2,900 mg/m^3.[184]

The pulse rate of dogs was decreased during exposure to 522-580 mg/m^3 and higher concentrations.[17]

Temperature. After lethal exposure of dogs to chlorine, the body temperature decreased from a normal of 39 C to about 35 C in 4 hr. Death followed, 12 hr after exposure. After less severe exposure, there was an initial decrease in temperature and a gradual recovery in 24 hr.[487]

Hemoconcentration. Underhill[486] found that the hemoglobin concentration in dogs severely poisoned with chlorine increased to as high as 178% of normal. In some that survived, the concentration reached 145% of normal during the pulmonary edema stage.

Blood Pressure. The blood pressure in dogs and cats decreased soon after exposure to chlorine, during the period of bradycardia.[22,58,214] The decrease occurred before edema or asphyxia and was accompanied by constriction of the splanchnic vessels.[22] The pressure remained low when edema was fully developed. As death approached, the pulse became rapid and the blood pressure decreased to the point of shock.

Blood Oxygen. Bunting et al.[58] exposed dogs for 30 min to chlorine concentrations of 1,970-2,840 mg/m^3. The oxygen saturation of arterial blood decreased from a normal 98% to 60-67% 10 min after exposure. Immediately after a 30-min exposure of dogs, Underhill[486] found that the venous oxygen concentration had decreased from 12.1-15.5 vol % to 6.2-8.2 vol %.

Acid-Base Balance. The effects of inhaled chlorine on acid-base balance have been studied in dogs. Immediately after a 30-min exposure to concentrations of 1,670-3,330 mg/m^3, acidosis was seen. The pH was reduced from 7.2-7.33 to 6.96-7.03. There was a moderate increase in carbon dioxide tension and a slight reduction in bicarbonate concentration.[58]

In animals that were mildly affected, the acid-base displacement returned to normal in 5-7 hr. In one dog, the acidosis persisted even after 19 hr.

Changes in urinary excretion were correlated with those effects.[487] There was an increase in urinary acidity and an increase in excretion of ammonia acid phosphates. Excretion of total nitrogen, creatinine, and uric acid was increased, especially on the second day after exposure. Chloride excretion was decreased at the time of hemoconcentration and increased after later dilution. Hjort and Taylor[220] also reported a rapidly increasing acidosis in dogs exposed for 2-7 hr to chlorine at 2,400 mg/m^3 (800 ppm).

Cause of Death. Underhill[487] attributed death to pulmonary edema and hemoconcentration. He considered the former as only an indirect cause of death. The conclusion was based on the knowledge that maintenance of increased oxygen concentration in the arterial blood (above normal) did not prevent death. Some animals died with much less edema than others, and some survived with an "apparent excessive quantity of fluid in the lungs." When hemoconcentration was prevented, animals survived, despite pulmonary edema.

Pathologic Findings after Single Exposures

Mice. In the studies of Silver *et al.*,[434] mice were exposed to various concentrations of chlorine for 10 min. Most deaths were attributed to pulmonary edema. In some, death occurred with slight edema accompanied by congestion; in others, death seemed to be related to secondary pneumonia. Klotz[278] found thrombi in arterioles, venules, and capillaries of mice after chlorine exposure.

Dogs. Sudden death during exposure to high concentrations of chlorine has been noted in dogs and men.[286,498] This has been attributed to respiratory reflexes.

Dogs that died 1½ min after exposure to high concentrations of chlorine were autopsied immediately.[286] The peripheral vessels did not bleed. The lungs were retracted to about one-third of the chest cavity. They were greenish-gray and like India rubber in appearance and consistency. On section, they were greenish-gray, dry, bloodless, and friable. The trachea and bronchi were gray and dry. The heart was dry and in systole. The right side of the heart was slightly dilated and contained thick blood.

In dogs that died 1-24 hr after exposure, the smaller bronchioles were constricted, with almost complete closure of the lumen.[518] It has been suggested that the constriction might have resulted from sectioning of the lung.[290]

In dogs that died 48 hr after exposure, there was necrosis of the epithelial lining cells of the trachea, the bronchi, and the walls of the alveoli that communicated directly with the terminal bronchioles. The affected epithelial cells were eosinophilic, and the nuclei were pyknotic. Cell death was indicated by nuclear staining with trypan blue. A layer of fibrin coated the surface of the trachea or bronchi where the necrotic epithelium had sloughed. Stripped-off sheets of epithelium often blocked the bronchiolar lumen. Most of the alveoli were filled with edematous fluid; others were emphysematous. Fibrin was deposited on many alveolar walls. Alveolar capillaries were congested, but no thrombi were found.[518]

The edema had begun to subside 2-4 days after exposure. At that time, pneumonia was noted in 95% of the dogs.[290,518] Acute inflammation was noted on the surface and in the cells of the trachea and bronchi. The pneumonia was peribronchial or lobular. Bronchioles were often obstructed by fibrin exudates, and the alveoli were atelectatic. Rapid regeneration had occurred in the epithelial linings of some bronchioles, the bronchi, and the trachea.

In dogs that died 5-10 days after exposure, pneumonia and abscesses were common. Winternitz et al.[518] and Lambert[290] showed that organisms normal to the mouth invade the lungs after chlorine poisoning.

Animals that died or were sacrificed 15 and 193 days after exposure had patchy emphysema and atelectasis.[290,518] The latter was associated with mucopurulent plugs and chronic inflammatory changes in the bronchi. There were also obliterated bronchioles surrounded by pneumonia. Poor physical condition often accompanied the more extensive pulmonary lesions. Dogs that made good recovery had few or no pulmonary lesions at the time of sacrifice.

Koontz reported insignificant scars and areas of organization and hemorrhage in dogs sacrificed 14-20 weeks after exposure.

Effects of Repeated Inhalation or Ingestion

Lethality of Exposure for 3 Days. Mice were not killed by being exposed to chlorine at 2.5-10 ppm 8 hr/day for 3 consecutive days.[385]

Resistance to Disease. Repeated inhalation by rabbits and guinea pigs of chlorine at 5 mg/m^3 (approximately 1.7 ppm) for 1 hr daily for several days caused deterioration of the nutritional state, blood alterations, and decreased resistance against infections. Under similar experimental conditions, a concentration of 2 mg/m^3 (approximately 0.7 ppm) was not toxic.[148]

Repeated exposure of rabbits to 2-5 mg/m^3 over periods of up to 9 months caused weight loss and increased incidence of respiratory disease.[436]

In guinea pigs, the inhalation of small quantities of chlorine accelerated the course of experimental tuberculosis.[12]

Other authors have reported on guinea pigs with experimental tuberculosis that were exposed to chlorine in air diluted 1:200,000 for 2-4 months. The gas did not seem to influence the development of the disease.[110]

Pulmonary Disease in Rats. Various studies have been done on rats with spontaneous pulmonary disease (SPD) and specific-pathogen-free (SPF) rats to evaluate differences in response to chlorine.[25,130,281] Rats with SPD were compared with similar rats that had been exposed to chlorine. The disease is characterized by goblet cell proliferation, excessive mucus secretion, and focal damage to the lung periphery. Exposure to chlorine accelerates the course of the disease process.[130] SPF rats show very few goblet cells and no lymphoid cuffing. The SPF animals tolerate higher doses of chlorine than the diseased (SPD) animals. After exposure to chlorine, the lungs of the diseased animals show changes that resemble human chronic bronchitis more closely than the lungs of the SPF rats.[25]

Thirty female rats weighing 120-140 g were exposed to the air in a chlorine factory for 5 hr/day for 4 months. The upper respiratory tracts became inflamed, and body weights were lower than those of controls. Early leukocytosis was followed by leukopenia on termination of the experiment, at which time the estrus cycles were longer, and fertility and the number of animals in estrus were lower.[3]

Multigeneration Test. Water containing chlorine at 100 mg/liter was well tolerated when drunk over the whole life span by 236 BDH rats in seven consecutive generations. There were no toxic effects on fertility, growth, blood, or as observed in the histology of liver, spleen, kidneys, or other organs. The incidence of malignant tumors was the same in control and experimental animals. The life span was not influenced.[112]

Reproduction in Rabbits. Sklyanskaya and Rappoport exposed animals to chlorine in air at concentrations of 0.002-0.005 mg/liter for 9 months.[436] Six rabbits produced normal offspring. In two cases, macerated fetuses were found in the peritoneal cavity.

EFFECTS OF CHLORINE ON MAN

Scheele of Sweden first prepared chlorine gas in 1774.[303] Because it was liberated from hydrochloric acid and thought to contain oxygen, it was called oxymuriatic acid gas. Others, because of the then popular phlogiston theory, referred to it as dephlogisticated muriatic acid. In the early 1800's, Sir Humphry Davy considered the elemental character of the material, and the term "chlorine" (from the Greek "chloros," meaning yellowish green) was coined.[105]

Not long afterward, the medical implications of the gas were recognized. In 1824, Dr. William Wallace of Dublin published a work entitled "Researches Respecting the Medical Powers of Chlorine Gas."[438] Kastner, obviously aware of the adverse effects of the material, in 1825 produced an article about an "Antidote for Inhalations of Chlorine."[265] A series of laboratory and field observations have followed.

A wide variety of effects have been reported to be associated with acute and chronic exposures to chlorine gas: cough, conjunctivitis, fever, headache, anorexia, nausea, vomiting, befuddled sensorium, pulmonary edema, anxiety and other neuroses, anosmia, tuberculosis, nephritis, bronchitis, asthma, pneumonia, pleurisy, meningitis, chronic tachycardia, neurocirculatory asthenia, chronic laryngitis; valvular heart disease, keratitis, acne, dental caries, and pulmonary fibrosis. Some are, some probably are not, related to chlorine exposures.[19,31,287]

Experimental Observations

Determinations of Odor and Irritation. Although much of the experimental work has been done with animals, some controlled studies have been made with human volunteers. Matt, in the late 1800's, stated that it was possible to work uninterruptedly in the presence of chlorine at 1-2 ppm.[100,148] Vedder and Sawyer, in 1924, published dose-response data that they had determined experimentally with human volunteers.[498] They listed the concentrations and durations of exposure that produce various effects--from odor detection to death (0.01-3.0 mg/liter). They did not elaborate on how they had determined human death experimentally. Beck, in 1959, reported on odor threshold of 0.15 mg/m^3 (0.05 ppm) and noted the possibility of adaptation.[24] Leonardas *et al*., in 1968 reported the odor threshold as 0.314 ppm.[299] Aside from the reports from eastern Europe, much of the dose-response information from other work seems to be related to these studies.

Russian Test Techniques. The Russians have published some of the data on human responses to chlorine. Their studies are interesting, but care must be taken in interpreting their data, because they use concepts and methods alien to most scientists trained in the West. Even in their work on the physiologic responses of odor and irritation, their protocols are sufficiently different from those of other scientists to make the direct comparison of threshold values difficult.

They seem to attach great significance to the reflex effects of chlorine--changes in higher nervous activity. Although they regard such changes as protective adaptational reactions, and not pathologic in the true sense of the word, they assert that such effects "prove" that conditions have deviated from the physiologic optimum and that the organism is thus being adversely affected by the environment.[395] Many western scientists disagree with this interpretation and doubt the value of such studies.

The following is a brief discussion of some of the Russian test techniques. In some cases, effects are noted below the Russian-recognized odor threshold. It has been suggested that this is related to which nerve endings are stimulated--olfactory or trigeminal (odor or irritation).

- Odor Threshold: Reproducibility of odor threshold is reported to have been obtained by means of a cylinder pair (Figure 5-1). The apparatus is arranged to allow a trained observer to make rapid comparisons between clean air and various calibrated concentrations of a chemical. On the basis of this method, the odor threshold of chlorine is reported to be 0.7 mg/m^3.[456]

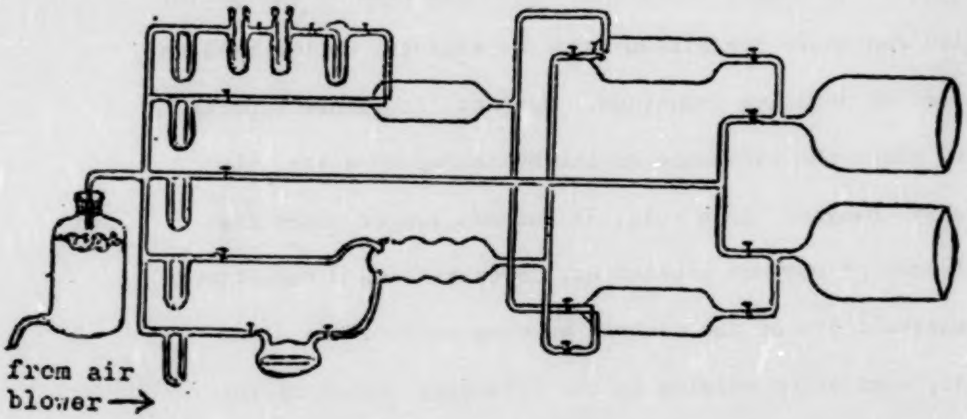

FIGURE 5-1. Schematic drawing of apparatus for determination of odor threshold concentration. (Original sketch of inhalation setup does not itemize components.) (Reprinted from Styazhkin.[456])

- Respiratory Tract Responses: Changes have been noted in the rhythm, frequency, and amplitude of respiration after exposures to chlorine gas. They develop apparently only at concentrations perceived subjectively as odor or irritation. At lower concentrations, no effect on respiration is reported to occur.[395,456]

- Optical Chronaxy: Chronaxy is a measure of the excitability of nervous or muscular tissue. It is the minimal time that a current of twice the threshold strength (the rheobase) must flow to excite a tissue. To measure optical chronaxy, an electrode is placed on the orbit of the eye near the upper lid, and a baseline is established, with phosphene (a sensation of light) as the desired response. Simultaneous inflation of a chemical may produce a shift in the baseline. According to Pavlov's teachings, excitation of the cerebral cortex in one region can cause inhibition in other regions, on the basis of the law of negative induction. Russian literature reports that, under the influence of the breathing of a gas, the chronxy changes: as a rule, it becomes longer under the influence of odorous substances, demonstrating a reduction in excitability of the central nervous system. In other words, excitation arising in the olfactory region of the cerebral cortex causes inhibition of the visual region. This change disappears quickly on cessation of olfactory stimulation. Chlorine does not affect chronaxy at concentrations equivalent to odor threshold.[395,457]

- Visual Adaptometry: The ability to distinguish a light signal in darkness can be defined in terms of threshold luminosity, as well as rapidity of adaptation in darkness. Simultaneous or previous exposure to a chemical may alter visual performance, according to the Russian literature. The visual adaptometry test demonstrates one of the problems of Pavlovian doctrine: moderate stimuli tend to increase and stronger stimuli tend to reduce neural activity. With some substances, such as sulfur dioxide and furfural, changes in light sensitivity may be noted at concentrations only one-third of the odor threshold. With chlorine, alterations are noted only at concentrations perceptible by smell.[395]

- Plethysmography: The inhalation of a chemical may be monitored by plethysmographic techniques--that is, by encasing a finger in a volume-sensing device or plethysmograph. Volume change depends on the vascularity of the tissues. Chlorine does not appear to affect the vascularity of peripheral tissues at the lower ranges of exposure related to odor threshold.[395]

Additional Russian techniques are used in behavioral toxicology--particularly conditioned reflex measurements. It is uncertain, however, whether chlorine significantly affects such tests.[395]

In conclusion, this array of measurements of physiologic responses adds little to the interpretation of the effects of chlorine at low concentrations. It appears likely that significant biologic effects of exposure to chlorine at relatively low concentrations are confined to odor and mucous membrane irritation.

Treatment of Respiratory Diseases. Smith, in 1893, discussed the possibility of "disinfecting human beings with chlorine and bromine".[439] Kuster, in 1915, reportedly used chlorine successfully to "cure" meningococcus and diphtheria carriers.[498] Army medical officers noted that, after the introduction of chlorine as a war gas in 1915, there seemed to be decreased respiratory problems among front line troops.[165] Baskerville, in 1919, was of the opinion that small amounts of chlorine decreased the incidence of respiratory diseases among workers.[19] In 1922, a study was done in Camp Perry, Ohio, using chlorine gas for the treatment of the common cold and bronchitis, with reportedly good results.[165]

Vedder and Sawyer did follow-up studies on the Camp Perry study and made observations on chlorine workers at Edgewood Arsenal during World War I. It was noted during an influenza epidemic that the post's chlorine workers had decreased morbidity, compared with workers not routinely exposed to chlorine gas. On the basis of their experiments, they believed that chlorine at 0.015-0.020 mg/liter (5-7 ppm) inhaled for an hour had a "distinctly curative value in common colds, influenza, whooping cough, and other respiratory diseases in which the infecting organisms are located on the surface of the mucous membranes of the respiratory passages."[498] The key, they thought, was for the exposure to be of sufficient strength and duration to produce a concentration of 1 ppm on the fluid lining the respiratory tract.[498]

In addition to the over 930 patients treated by Vedder and Sawyer, Gilchrist reported in 1924 on another 900 patients who were so treated, again with allegedly good results. It must be noted that, in Gilchrist's study, cure or improvement was based on patient history, not medical examination.[165]

Field Observations

Some studies on the effects of chlorine exposure have been done under controlled circumstances with medical observation during the course of the exposure, but the bulk of the material on the effects has been derived from studies of chlorine exposures "in the field": war gases during World War I, catastrophic accidents, chronic industrial exposure, and industrial hygiene surveys. Aside from the latter, in which trained observers were exposed during the course of field measurements of chlorine, it is often difficult to reconstruct the exact degree of exposure and thus determine accurate dose-response data.

Acute Exposures During World War I.

The effects of chlorine on man were not generally recognized by either the public or the scientific community until after its introduction as a war gas on April 22, 1915.[168] Although it was replaced by other agents after being used by both sides several times, the labels "war gas" and "poison gas" persist.

During the initial attacks, many of the Allied troops, unprepared and unprotected, were victims of chlorine gassing. The exact number is difficult to determine, because the British originally listed deaths from this cause under the general heading of "killed in action." Gilchrist and Matz reported that the U.S. War Department determined that 70,752 men, were casualties as a result of gassing, including 1,843 with chlorine.[168]

Among the 1,843, few deaths occurred. Because of disagreement as to what pathologic effects chlorine could be related to, there was and is less than universal agreement as to the number of disabilities attributable to gassing during World War I. The government apparently accepted a number of cases of tuberculosis, cardiovascular disease, and nephritis as being related to wartime exposures to chlorine. Even so, the number was small.[168]

Meakins and Priestly examined 700 Canadians some 4 years after they had suffered massive chlorine exposure; 16.4% were found unfit for work, 11% because of heart trouble and 3.5% because of asthma or bronchitis.[338]

There are other studies of victims of war gases by British, French, and American investigators. Most of the retrospective analyses mention bronchitis, emphysema, and other respiratory problems as possible sequelae of chlorine exposures.

Catastrophic Accidental Exposures. A number of catastrophic accidental exposures to chlorine have occurred, both here and abroad. Some incidents involved individuals, and others, large groups.

In 1947, approximately 1,000 persons were exposed to high concentrations of the gas when a chlorine cylinder leaked into a ventilator of a Brooklyn subway. Some 208 required hospitalization, and 33 of these were followed for 16 months. There were no deaths, and, by the methods used for evaluation, none had detectable residual damage.[73]

Approximately 150 longshoremen were exposed during an accident in Baltimore in 1961. A number of them had follow-up of 2-3 years. The authors believed that there were indications of permanent damage. No deaths occurred.[282]

The derailment of a freight train near a small Louisiana community in 1961 caused 6,000 gal of liquid chlorine to spill. A low wind dispersed the cloud of gas over an area of several square miles; 7 hr after the accident, concentrations up to 400 ppm could be detected 75 yards from the wreck area, at a location considered only "moderately contaminated." Of the 100 people affected, 17 were hospitalized. An 11-month-old died with pulmonary edema. From 3 to 7 years after exposure, 12 of the victims were studied. Chest X ray did not reveal significant abnormality. All subjects were free of symptoms, except a 53-year-old man, a heavy cigarette-smoker with evidence of pulmonary emphysema. Occasional blood-gas abnormalities and marginal pulmonary-function values were noted, but the authors could not refer them to injury experienced at the time of the accident. Rather, cigarette-smoking, obesity, and pregnancy appeared to be the relevant factors.[253,511]

Seven chemical workers, exposed in separate accidents, have been studied by Beach et al.[23] Although all recovered completely, three experienced respiratory failure, and all presented radiographic evidence of pulmonary congestion. In one case, extensive pulmonary edema cleared after several days. Six of the seven underwent spirometry and measurement of lung volume and transfer factor 8 weeks after discharge; only one had an obstructive pattern, with increased residual volume and normal diffusion, and the other five had values within normal ranges.[23]

In 1969, fumes leaked from a filtration plant in Cleveland, killing two people. Kaufman and Burkons studied 18 of the 35 affected and found that a single acute exposure did not result in measurable permanent clinicophysiologic abnormality.[270] Adelson and Kaufman reported on the two that died. Abnormalities were noted in the lungs of both and in the kidneys and brain of the one who survived longer.[1]

In 1968, Dixon and Drew reported the death of a chemical worker who was exposed to chlorine for about 30 min. Death was attributed to pulmonary edema.[108]

The Washington Post reported, in 1971, that 36 people were hurt by inhaling chlorine fumes at a swimming pool.[106]

Similar reports have come from Europe. Romcke and Evensen reported on the explosion of a railway tank containing 15 tons of chlorine in Mjondalen, Norway; 85 people were injured, and three died.[403] Hoveid did a follow-up study some two decades later and concluded that the after-effects in the survivors were few and trivial.[228]

Eight people died and 241 were injured in a cellulose factory in Walsum, Germany, when a tank broke and released 17 tons of liquid chlorine.[14]

Chronic Exposures in Industry. Some population groups, notably industrial workers, are chronically exposed to chlorine. A number of reports have discussed the correlation of pathologic effects with chronic exposure to low concentrations. Documentation of the threshold limit values notes that the older literature states that a concentration of around 5 ppm causes respiratory complaints, nasal mucous membrane inflammation, increased susceptibility to tuberculosis, and corrosion of the teeth in workers chronically exposed.[7]

In 1967, Ferris et al.[142] noted that men working with chlorine had somewhat poorer respiratory function and more shortness of breath than those working with sulfur dioxide, but that both groups had a lower prevalence of respiratory disease than that of the local male population. They appreciated the phenomenon of self-selection; those in the general population with respiratory disease would actively avoid jobs that would aggravate their symptoms.

Chester et al.[75] noted that the immediate effect of acute chlorine exposure, an obstructive ventilatory defect, cleared rapidly, but that workers chronically exposed seemed to have a decreased maximal midexpiratory flow. This was most marked among chlorine workers who smoked.

In a study of 332 chlorine-cell workers, generally exposed to less than 1 ppm, Patil et al.[373] found no statistically significant signs of symptoms on a dose-response basis.

Industrial Hygiene Surveys. Trained industrial hygienists have recorded their subjective responses to chlorine and have attempted to correlate them with simultaneous measurements (Table 5-9). These were not controlled experiments, but casual observations during the course of regular work. Apparently, no attempt was made to find the thresholds of the various responses. The results are nonetheless interesting.

It should be noted that observations made by the same person late in the day after previous exposure are frequently less discerning than those made earlier in the day (H. R. Hoyle, personal communication), indicating possible adaptation. This acclimation was not as pronounced as has been noted with other chemicals, such as ammonia; the differences in concentration for similar subjective responses between the industrial hygienist, with relatively short exposures, and the workman on the job, with more chronic exposures, were not great.

It is interesting to note in Table 5-9 the overlap for odor between "none" (0.08-2.9 ppm) and "strong" (2.2-41 ppm) and the overlap for respiratory irritation between "none" (0.08-2.9 ppm) and "intolerable" (2.6-41 ppm). The difficulty of constructing a dose-response relationship from symptomatology alone, as was attempted by Hoveid, can be appreciated.[228]

Immediate Effects of Acute Exposure

The immediate effects of chlorine exposure are basically odor and irritation. The odor threshold has been reported in western literature to be as low as 0.02 ppm[379] and as high as 3.5 ppm.[105] Comparable figures in Russian literature are 0.1 mg/m^3 (0.03 ppm) and 3 mg/m^3 (1 ppm).[485] Minimal

TABLE 5-9

Subjective Responses to Chlorine[a]

Odor	No. Air Samples	Chlorine Concentration in Air, ppm Range	Average
None	65	0.08- 2.9	1.2
Minimal	16	1.1 - 2.7	1.6
Easily Noticed	12	1.9 - 3.5	2.5
Strong	29	2.2 -41	8

Respiratory Irritation	No. Air Samples	Chlorine Concentration in Air, ppm Range	Average
None	81	0.08- 2.9	1.3
Minimal	7	1.95- 2.9	2.6
Painful	11	1.92- 4.23	3
Intolerable	23	2.6 -41	9

Eye Irritation	No. Air Samples	Chlorine Concentration in Air, ppm Range	Average
None	81	0.08- 2.9	1.3
Minimal	1	--	7.7
Painful	4	8.7-41	20

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[a] Data from H. R. Hoyle, personal communication.

mucous membrane irritation has been reported in western literature from 0.2[379] to 16 ppm,[498] and in Russian literature, from 1 to 6 mg/m^3 (0.3-2 ppm).[464]

Man's olfactory organ, although less sensitive than that of many lower animals, is able to react to some substances diluted to picograms (10^{-12}g) per liter of air. This sensitivity varies with the odor, with the individual, and, in some cases, with the duration of exposure. A person exposed to relatively low concentrations of chlorine may rapidly lose the ability to detect its odor, so potentially harmful concentrations of chlorine may not cause sufficient odor or irritation to give adequate warning and alert the person to avoid the exposure. Laciak and Sipa[287] concluded that chlorine workers had significant olfactory deficiency, which increased with length of employment, and that workers with lower olfactory efficiency suffered intoxication more often and more severely.

Vedder and Sawyer[498] determined experimentally the concentrations at which the odor of chlorine was plainly perceptible 0.010 mg/liter (3.3 ppm) and at which slight irritation of the throat was noted after exposure for 1 hr 0.02 mg/liter (6.6 ppm) and after 3 min 0.048 mg/liter (16 ppm). Hoyle (personal communication) reported that odor threshold concentration varied from 1.1 to 2.7 ppm (average, 1.6 ppm), that respiratory irritation threshold concentration varied from 1.95 to 2.9 ppm (average, 2.6 ppm), and that the eye irritation threshold concentration was 7.7 ppm. De Nora and Gallone[105] gave 1.0 ppm as the lowest concentration that would cause slight symptoms after exposure for several hours, 3.5 ppm as the odor threshold concentration, 4.0 ppm as the highest concentration that can be breathed for 1 hr without serious effects, 15.1 ppm as the throat irritation threshold concentration, and 30.2 ppm as the coughing threshold concentration. Petri[379] reported that the odor or taste threshold concentration is 0.02-0.05 ppm and the respiratory or eye irritation threshold concentration is 0.2-0.5 ppm. Leonardas et al.[299] reported an odor threshold concentration of 0.314 ppm; this was the lowest concentration at which all four members of a panel could positively recognize the odor of chlorine.

Joyner[253] reported minor first-degree burns of the skin secondary to chlorine vapor exposures, but did not estimate concentrations or durations of exposure.

In the Russian literature, Takhirov,[464,465] reporting on 238 tests made on 11 test subjects, noted that the minimal perceptible chlorine concentration ranged between 0.8 and 1.3 mg/m^3 (0.25-0.4 ppm), with the average being 1 mg/m^3 (0.3 ppm). He also reported that the maximal nonperceptible chlorine concentration was 0.7-1 mg/m^3 (0.2-0.3 ppm), with the average being 0.8 mg/m^3 (0.25 ppm). In all test subjects, the odor of chlorine was clearly perceived at 3-4 mg/m^3 (1-1.3 ppm); at such concentrations, all subjects had acute irritation of upper respiratory mucosa, and some had a reflex cough and conjunctival irritation. At 1.3-2 mg/m^3 (0.4-0.6 ppm), most noted the chlorine odor and had slight nasal irritation, and some complained of conjunctival irritation. Some complained of slight nasal irritation at even lower concentrations.

Styazhkin[456] reported 0.7 mg/m^3 (0.2 ppm) as the chlorine odor threshold concentration. Lazarev[485] cited 3 mg/m^3 (1 ppm) for odor and 1-6 mg/m^3 (0.3-2 ppm) for mucosal irritation. Ugryumova-Sapozhnikova[485] concluded that the olfactory organ can "sense" a chlorine concentration of 0.3 mg/m^3 (0.1 ppm) and stated that others had reported the "sensing" concentration at 0.1-0.5 mg/m^3 (0.03-0.2 ppm).

At higher concentrations, the irritation becomes pronounced, with marked cough, dyspnea, and conjunctivitis. At sufficiently high concentrations, pulmonary edema or even death may occur. Some of the victims of chlorine exposure during World War I had minimal to no significant pathology of their lungs, as determined by autopsy. It was postulated that they died as a result of laryngeal spasm secondary to sudden large exposure to irritating chlorine gas.[168]

Zielhuis[528] stated that 30 ppm for 30 min was potentially lethal. Vedder and Sawyer[498] reported that 0.30 mg/liter (100 ppm) was tolerable for only a few seconds and that 30 min of exposure at 3.0 mg/liter (1,000 ppm) was lethal. De Nora and Gallone,[105] however, reported that 40-60 ppm was dangerous in exposures of 30-60 min and that 1,000 ppm would be fatal after but a few deep breaths.

Latent Effects and Sequelae of Acute Exposure

Asthmatic people often display acute bronchospasm or bronchial obstruction when exposed to nonspecific respiratory irritants. The occurrence of asthma, or rather the aggravation or relapse of asthma, in conjunction with exposure to chlorine is seldom reported in the literature.[421] It is of interest that not only has inhalation of low concentrations of chlorine caused an asthmatic attack, but ingestion of chlorinated water has been associated with the occurrence of asthmatic relapse.[506] Sheldon and Lovell[421] refer to a 53-year-old asthmatic housewife. Each time she visited an indoor swimming pool, she experienced severe asthma within a few hours after being exposed to the air contaminated by the swimming-pool water, which had a chlorine load of 4-6 ppm. This patient once developed such an extreme attack of wheezing within an hour of entering the pool area that she was forced to leave the building, thus immediately obtaining relief. Her asthmatic complaints increased on Monday nights, after her weekly washing with a liquid chlorine rinse. When she discontinued the chlorine rinse, she experienced no further aggravation.

Hoveid,[228] in his follow-up study of the chlorine gas accident in Mjondalen, Norway, using symptomatology and dose-response data from U. S. Bureau of Mines Technical Paper 248, attempted to derive relative exposure doses of the victims. He believed that all those hospitalized were exposed to concentrations of at least 30 ppm and that many were exposed to 60 ppm. He concluded that the after-effects, some two decades after exposure, were few and generally trivial; the most common complaint was dyspnea. A number of authors are of like opinion, that single acute exposures cause no permanent damage.[228]

Other authors disagree. Kowitz _et_ _al_. studied the accident in Baltimore in which 150 longshoremen were accidentally exposed to chlorine. They felt that sufficient abnormalities of pulmonary function were found to suggest permanent damage.[282] Weill _et_ _al_., on review of their data, disagreed.[511]

There is disagreement as to whether pulmonary edema, when it occurs, has its onset immediately after exposure or is delayed.[146] There is also some disagreement as to the role of chlorine inhalation in the development of pulmonary infections. Pneumonia and infectious bronchitis have been reported, as has tuberculosis, but many authors doubt the role of chlorine in the latter disease.[168,511]

The immediate effect of exposure of the respiratory surface to chlorine may be involvement of the most distal airways and may persist as latent sequelae, which are not readily documented by most routine tests of function. For instance, in 19 subjects (mean age, 35.3 years) who were accidentally exposed to chlorine several weeks (mean, 3.5 months) before testing, the most common abnormal pulmonary function was closing volume.[63] The closing volume test has been introduced in recent years,[66] and appears to be a most sensitive measure of disorder of the peripheral (or "small") airways.[334]

Pathology of other organ systems has also been reported. Gastric ulcers, when they occur, may be stress ulcers and not result from the direct action of chlorine on the gastric mucosa.[194] Changes in brain and kidney tissue of victims who die a couple of days after exposure may be due to hypoxia associated with pulmonary edema, rather than a direct toxic effect of the gas.[1] The development of valvular heart disease is questionable. Chlorine produces its effect by localized reaction, and no systemic effects are thought to occur.

Both liquid chlorine and gaseous chlorine can produce ocular damage. The production of any changes in the internal structures of the eye, however, is not reported to have occurred in either acute or chronic exposure.[138]

Effects of Chronic Exposure

A number of authors have studied the effects of chronic exposures to low concentrations of chlorine. Ferris *et al.*[142] reported on observations made during the winter of 1963-1964 on a group of pulp-mill workers exposed to chlorine and oxides of chlorine in the process of bleaching pulp. They were compared with workers who were exposed to sulfur dioxide. The population was observed during a 2-month period with the use of a respiratory questionnaire, simple pulmonary-function tests, and environmental determinations. The average cumulative exposure duration was 20.4 years. The chlorine concentrations during the surveillance period were reported to be around 0.001 ppm. But they were known to have peaked as high as 64 ppm before the study, so the target population represented a mixture of people with acute and chronic low-concentration exposures to chlorine and oxides of chlorine. The authors did not consider the difference between the two groups to be statistically significant. There was significantly less respiratory disease in the total mill population than in the general male population of the town. They did not consider the low prevalence of disease in the working population indicative of the "safety" of the pollutants to the general population.

McCord[7] reported on a case of chronic intoxication in a worker chronically exposed to chlorine at concentrations up to 15 ppm.

Kaufman and Burkons[270] noted that workers with occupational exposures to chlorine of 5-30 years had persistent obstructive airway defects and mild hypoxemia.

Chester _et_ _al_.[75] studied workers who, for the most part, had chronic exposures to chlorine at less than 1 ppm; some of them, on occasion, had acute exposures of sufficient dose to require oxygen therapy (>30 ppm ?). Three of 139 had significant impairment of ventilatory function. Compared with controls, the exposed group had a significant reduction in maximal midexpiratory flow. This was even more marked when an exposed group of smokers was compared with a control group of nonsmokers. This may indicate that smoking and chlorine exposure have additive or synergistic noxious effects. The authors suggested that the changes seen in their patients and in those of Kowitz _et_ _al_.[282] could represent peribronchial cicatrization secondary to chlorine inhalation.

Patil _et_ _al_.[373] studied 600 diaphragm-cell workers in a number of chlorine manufacturing plants in North America. Exposure data and medical evaluations--including chest X ray, electrocardiogram, pulmonary-function tests, and physical examinations--were collected for 332. On a time-weighted average, exposures ranged from 0.006 ppm to 1.42 ppm; most were exposed to less than 1 ppm. By history, tooth decay showed a moderate degree of dose response, but this was not confirmed by examination. The authors believed that no statistically significant signs or symptoms on a dose-response basis were found. Some minor hematologic changes were noted, as were some symptoms, such as nervousness, shyness, and anxiety. The authors were not convinced that the latter were associated with chlorine exposure itself, but thought that they might be due to some other factor in the chlorine-cell room.

In light of this, it is interesting to note that the victim of an accidental chlorine exposure often exhibits a variable degree of acute anxiety.[75,165] This anxiety is lessened if the patient is treated calmly and with confidence.[283] It has been observed that the industrial worker who has experienced multiple acute exposures does not manifest the high degree of acute anxiety as does the victim unaccustomed to chlorine.[283]

A number of authors have noted not only acute transient psychologic reactions, but also some longstanding problems. Chasis *et al.*[73] observed in 16 of 29 patients anxiety reactions with phobias, hysterical phenomena, and psychosomatic dysfunction for periods of 1-16 months after exposure.

Chloracne, a form of chronic skin lesion, has been reported among workers engaged in the production of chlorine by the electrolytic process. It is thought that a contaminant created by the reaction of chlorine with the tars in the anode cells produces the lesion, and not chlorine itself.[148] In confirmation of this, similar lesions are seen among those who are not exposed to chlorine gas but are working with various chlorinated aromatic hydrocarbons--the chloronaphthalenes, chlorophenyls, chlorophenols, etc.[96] The offending agents are thought to be reaction contaminants--various chlorinated dioxins.[274,329]

Finally, the phenomenon of tolerance, so often reported in the literature, should be mentioned. Sequential exposure appears to modify significantly the outcome of the individual response in some people.[291,431] The mechanism is not understood, although the same phenomenon has been described for a variety of irritant and toxic gases.[453] It has been noted that men may work without signs of discomfort in an atmosphere where the concentration of some irritants has accumulated gradually. The same atmosphere may be intolerable to persons entering the contaminated area from fresh air. When a "tolerant" person leaves the contaminated atmosphere for 10-30 min, the tolerance is lost, and reentry into the contaminated area is objectionable. The degree and duration of tolerance may be different for different irritants and for different concentrations.

Animal experiments indicate that development of a high degree of tolerance is possible. Jancso[243] and Porszasz and Jancso[383] have shown that, after serial injection of capsaicin, a strong irritant, into guinea pigs and rats, known irritants failed to produce their typical effects when applied to skin or eyes. The desensitization may persist for months.[244]

Chlorine gas recognition (odor) also appears to be influenced by previous exposure, in that the threshold concentration may tend to rise in prolonged or repeated exposure.[24,62] Perhaps related is the discrepancy in the literature in regard to those characteristics. For instance, observations gathered on chronically exposed workers seem to suggest an analogous tolerance with respect to both odor and mucosal irritation.[395,456]

Mutagenesis, Teratogenesis, and Carcinogenesis

There is no evidence of mutagenic, teratogenic, or carcinogenic effects of chlorine in human beings.

Pregnant women exposed to chlorine have gone to term with no reported complications. Women exposed to chlorine in their place of employment had normal pregnancy, delivery, puerperium, and lactation, and their infants were of normal weight.[435]

No increased incidence of lung or skin malignancies has been reported among chlorine workers.

Table 5-10 summarizes the available data on the threshold and limit values for chlorine, and Table 5-11 gives some examples of the available chlorine concentration limits.

Short-Term Public Exposure Limits (STPL's)

On the grounds that there is no justification for submitting the public to appreciable risk from chlorine in situations where exposures can be predicted, the NAS-NRC Committee on Toxicology has recommended "short-term public exposure limits." (Table 5-12). The Committee believes that none of these concentration-duration combinations presents any health hazard.

Public Emergency Limits (PEL's)

On the grounds that, under some emergency conditions, the public may be exposed to concentrations of chlorine in excess of the STPL's, the NAS-NRC Committee on Toxicology also recommended "public emergency limits." (Table 5-13). The human response to these combinations of concentration and duration may be perception of a strong odor or irritation of the mucous membranes, but the effect is thought to be reversible and to involve no serious sequelae.[356]

PHYSICAL STATES OF HYDROGEN CHLORIDE AND ROUTES OF EXPOSURE

Airborne hydrogen chloride exists in the anhydrous state and as a hydrochloric acid aerosol, i.e., as microdroplets of a solution of hydrogen chloride and water. Because anhydrous hydrogen chloride is highly hygroscopic, exposures to this material are potentially more dangerous to the biologic system than exposures to hydrochloric acid aerosols. It insults not only by corrosion, as does the acid, but also by desiccation.[411] This very affinity for water, however, makes general environmental chronic exposures to low concentrations of anhydrous hydrogen chloride extremely unlikely. Even in industrial settings, where anhydrous hydrogen chloride may be used in quantity,

TABLE 5-10

Summary of Chlorine Thresholds and Limits

Chlorine Concentration, ppm	Remarks	References
0.03-3.5	Range of reported odor thresholds	95, 299
1.0	TLV, OSHA time-weighted average	7, 490
1.0	Permissible concentration; 8-hr working day	246
1-2	Men can work without interruption	206
1-3	There might be slight irritation	528
3	Pennsylvania short-term limit for 5 min	377
3	Permissible excursion for 15 min based on TLV	7
3	Recommended as 60-min EEL[a]	528
3-6	Stinging or burning in the eyes, nose, and throat and perhaps headache due to sinus irritation; may be watering of eyes, sneezing, coughing, bloody nose or blood-tinged sputum	206
4	Recommended as 30-min EEL[a]	528
>5	Severe irritation of eyes, nose, and respiratory tract, which becomes intolerable for more than a few minutes	528
5	Recommended as 15-min EEL[a]	528
7	Recommended as 5-min EEL[a]	528
14-21	Dangerous for 0.5-1 hr	206
35-51	Lethal in 1-1.5 hr	151

---

[a] Emergency exposure limit; for an emergency in a manufacturing area and its neighborhoods, storage facilities, and surrounding areas, and during transport of the chemical; suggested by Zielhius in 1970.[528]

TABLE 5-11

Examples of Some Established Limits for Chlorine Concentration

	Reference
Threshold limit value (TLV): 3 mg/m^3 (1 ppm); for 15-min excursion; 9 mg/m^3 3 ppm	7
Russian maximal allowable concentration: industrial, 1 mg/m^3 (0.001 mg/liter)	239
Recommended EEL for submarine crews: 3 ppm for 60 min	357
Pennsylvania short-term limits: 3 ppm for 5 min	377
Maximal allowable concentrations in populated areas:	
Average 24-hr concentration, 0.03 mg/m^3 x 1,440	
Maximal single concentration, 0.1 mg/m^3 (Russian figures)	301
Recommended EEL's for occupational exposure:	377
60 min, 3 ppm 30 min, 4 ppm 15 min, 5 ppm 5 min, 7 ppm	
International MAC's in the workplace:	100
German Federal Republic, 2 mg/m^3 (1968)	
German Democratic Republic, 1 mg/m^3 (1963)	
Great Britain, 3 mg/m^3 (1955)	
Hungary, 1 mg/m^3 (1956)	
Poland, 1 mg/m^3 (1959)	
Yugoslavia, 3 mg/m^3 (1957)	
Czechoslovakia, 3 mg/m^3 (mean MAC, 1969) 6 mg/m^3 (peak MAC, 1969)	
Occupational Exposure Limits, Department of Labor, Occupational Safety and Health Administration: 3.0 mg/m^3 (1 ppm)	

TABLE 5-12

Short-Term Public Exposure Limits for Chlorine[a]

Duration, min	Chlorine Concentration, mg/m^3 (ppm)
10	2.9 (1.0)
30 and 60	1.4 (0.5)

---

[a] Values are tentative. The STPL's are to be considered time-weighted averages, with maximal excursion factors of 3 for the 10-min concentration and 2 for the 30- and 60-min concentration. Any excursions above the STPL should be compensated for by an appropriate reduction in the duration of the exposure. Adapted from National Academy of Sciences.[357]

TABLE 5-13

Public Emergency Limits for Chlorine[a]

Duration, min	Chlorine Concentration, mg/m^3 (ppm)
10	8.7 (3)
30 and 60	5.8 (2)

---

[a] Values are tentative. The PEL's are ceiling limits and are not to be exceeded. Derived from National Academy of Sciences.[357]

exposures to the anhydrous state are unlikely, because the material fumes in atmospheric humidity and forms the aerosol. Because of these hygroscopic properties, it must be assumed that published reports deal with hydrochloric acid aerosol unless they specifically state otherwise.

Exposures to gaseous hydrogen chloride are limited to the external surface of the body (integument and conjunctiva) and the lining of the respiratory tract (teeth and mucous membranes of the mouth, nose, pharynx, trachea, etc.).[322]

MECHANISMS OF ACTION OF HYDROGEN CHLORIDE

The mechanisms of action of hydrogen chloride may be conveniently described in two parts: molecular and elementary biochemical effects and disturbed function.

Molecular and Elementary Biochemical Effects

Hydrogen chloride is readily soluble in aqueous medium, up to concentrations of 72 wt %, at 20 C. It is also soluble, to a smaller extent, in organic solvents.[276] In water, hydrogen chloride dissociates almost completely, because its pK is -7. This occurs in the following fashion:

$$HCl + H_2O \rightleftarrows H_3O^+ + Cl^-$$

The hydrogen ion is readily captured by the water molecules, with production of hydronium ions, in which the proton is attached to the rest of the molecule by a coordinate covalent bond.[223]

Reciprocally, the hydronium ion becomes a donor of a proton, responsible in turn for a variety of reactions with organic molecules. For instance, protons, by virtue of their well-recognized catalytic property, may effectively cleave organic molecules.[28] Among others, hydrolysis of peptides and of esters may well assume major importance in the production of injury, inasmuch as these are components of the cellular wall. Furthermore, hydroxylation of carbonyl groups and polymerization, as well as depolymerization, of organic molecules are reactions caused by this catalytic property.[26,27]

With the loss of membrane integrity, the injured cell can readily be depleted of cytoplasmic components, and cellular death may follow rapidly. However, the dose-response relationships at realistic concentrations are not known.

Disturbed Function

Necrosis, or cellular death, is obviously the most serious functional effect of acid burn. Erythema and edema usually precede it, although edema is probably the most characteristic manifestation; it occurs in any tissue that bears the brunt of the exposure. Edema of the cornea and conjunctiva,[101] skin and surface mucosae,[315] and deep respiratory tissues has been described in connection with substantial or massive exposure.

Experiments with rodents suggest a discrepancy between animal species in regard to hydrogen chloride toxicity. Rats, for instance, survive at concentrations that are most effective in killing mice, guinea pigs, and rabbits.[101,315] Death is attributed principally to respiratory injury with emphysema, atelectasis, and pulmonary edema reflecting the extent of the damage.[101]

Residual alveolar injury may persist in animals sacrificed 14 days after exposure.[101] Differences in severity or type of injury have not been detected between aerosol and vapor phases of hydrogen chloride.[101] The environmental temperature seems to have some importance, with morbidity and mortality higher at 37 C than at 20.[298]

The genesis of pulmonary edema, including the variety caused by inhaled chemicals, has been reviewed recently.[399] Changes in permeability and liquid transport across cellular membranes are associated with histologically evident damage of the alveolar epithelium and endothelial cells.

The sequence of fluid accumulation, beginning around bronchioles and later involving alveolar spaces, has been well described by Staub.[448]

An analogy of the ultrastructural changes associated with hydrogen chloride inhalation has been described in association with aspiration of gastric juice.[5]

The effect of community exposure concentrations (i.e., air pollution) remains undocumented and hypothetical.

EFFECTS OF HYDROGEN CHLORIDE ON MAMMALIAN SPECIES OTHER THAN MAN

Single Exposures to Hydrogen Chloride Vapor and Aerosol

The effects of hydrogen chloride vapor on animals were reported as early as 1886 by K. B. Lehmann.[148] Lehmann's data are given in Table 5-14.

Darmer *et al.*[101] exposed mice and rats to hydrogen chloride vapor or aerosol for 5 or 30 min. The vapor concentrations were 3,200-57,290 ppm for 5 min and 410-6,681 ppm for 30 min. The aerosol concentrations were 6,571-62,042 ppm for 5 min and 1,204-6,640 ppm for 30 min. The LC_{50} values are shown in Table 5-15.

Gross examination of animals that died during or shortly after exposure revealed moderate to severe emphysema, atelectasis, and pulmonary edema. Recovery was not complete in animals that survived 14 days.

The lowest concentrations that caused death in these experiments by Darmer *et al.*[101] are shown in Table 5-16.

Dose-response regression lines calculated from the data of Darmer *et al.*[101] (Table 5-17) are shown in the Figures 5-2 through 5-9.

TABLE 5-14

Effects of Single Exposures of Hydrogen Chloride on Cats, Rabbits, and Guinea Pigs[a]

Animals	Hydrogen Chloride Concentration mg/m^3 (ppm)	Exposure Time, min	CT, mg-min/m^3	Effects
Cats and rabbits	150-210 (100-140)	Up to 360	54,000-75,600	Salivation, rhinorrhea, no sequelae
Rabbits and guinea pigs	2,000 (1,350)	75	150,000	Respiratory irritation, corneal opacity
	450 (300)	360	162,000	Cloudy cornea, catarrh
Rabbits and guinea pigs	5,000 (3,400)	90	450,000	Death 2-6 days after exposure

---

[a] Data from Lehmann.[148]

TABLE 5-15

LC_{50}'s of Hydrogen Chloride Vapor and Aerosol in Rats and Mice[a]

Animals	LC_{50}, mg/m^3 (ppm) 5 Min		30 Min	
Vapor:				
Rats	60,100[b]	(40,898)	6,900[b]	(4,701)
Mice	20,200[b]	(13,750)	3,900[b]	(2,644)
Aerosol:				
Rats	45,600	(31,008)	8,300	(5,666)
Mice	16,500	(11,238)	3,100	(2,142)

---

[a] Data from Darmer *et al.*[101]

[b] Values not given in original paper.

TABLE 5-16

Lowest Concentrations of Hydrogen Chloride Vapor or Aerosol that Caused Death in Experimental Rats and Mice[a]

Animals	Exposure Time, min	Lowest Concentration Causing Death mg/m^3 (ppm)	No. Deaths
Vapor:			
Rats	5	48,507 (32,255)	1/10
Mice	5	4,768 (3,200[b])	1/10
Rats	30	3,990 (2,678)	1/10
Mice	30	1,690 (1,134)	2/15
Aerosol:			
Rats	5	28,775 (19,312)	1/10
Mice	5	13,496 (9,058[b])	3/10
Rats	30	4,336 (2,910[b])	1/10
Mice	30	1,794 (1,204[b])	2/10

---

[a] Data from Darmer *et al.*[101]

[b] Lowest concentration tested.

TABLE 5-17

Bliss Dose-Response Regression Data for Lethality of Hydrogen Chloride Vapor and Aerosol in Mice and Rats[a]

Fraction Killed, %	LCt, mg-min/m^3			
	Vapor		Aerosol	
	Mice	Rats	Mice	Rats
	5-Min Exposures			
1	13,462	192,307	44,089	91,918
16	38,643	250,596	63,645	155,787
30	56,076	275,136	72,451	187,673
50	84,937	305,361	83,723	231,009
84	186,697	372,105	110,133	342,558
99	535,998	484,883	158,990	580,586
	30-Min Exposures			
1	29,994	109,157	28,653	119,081
16	65,754	158,819	57,171	179,381
30	86,763	181,303	72,950	207,319
50	118,187	210,135	95,747	243,615
84	212,369	278,034	160,384	330,825
99	465,640	404,490	319,918	498,360

---

[a] Data from Darmer *et al.*[101]

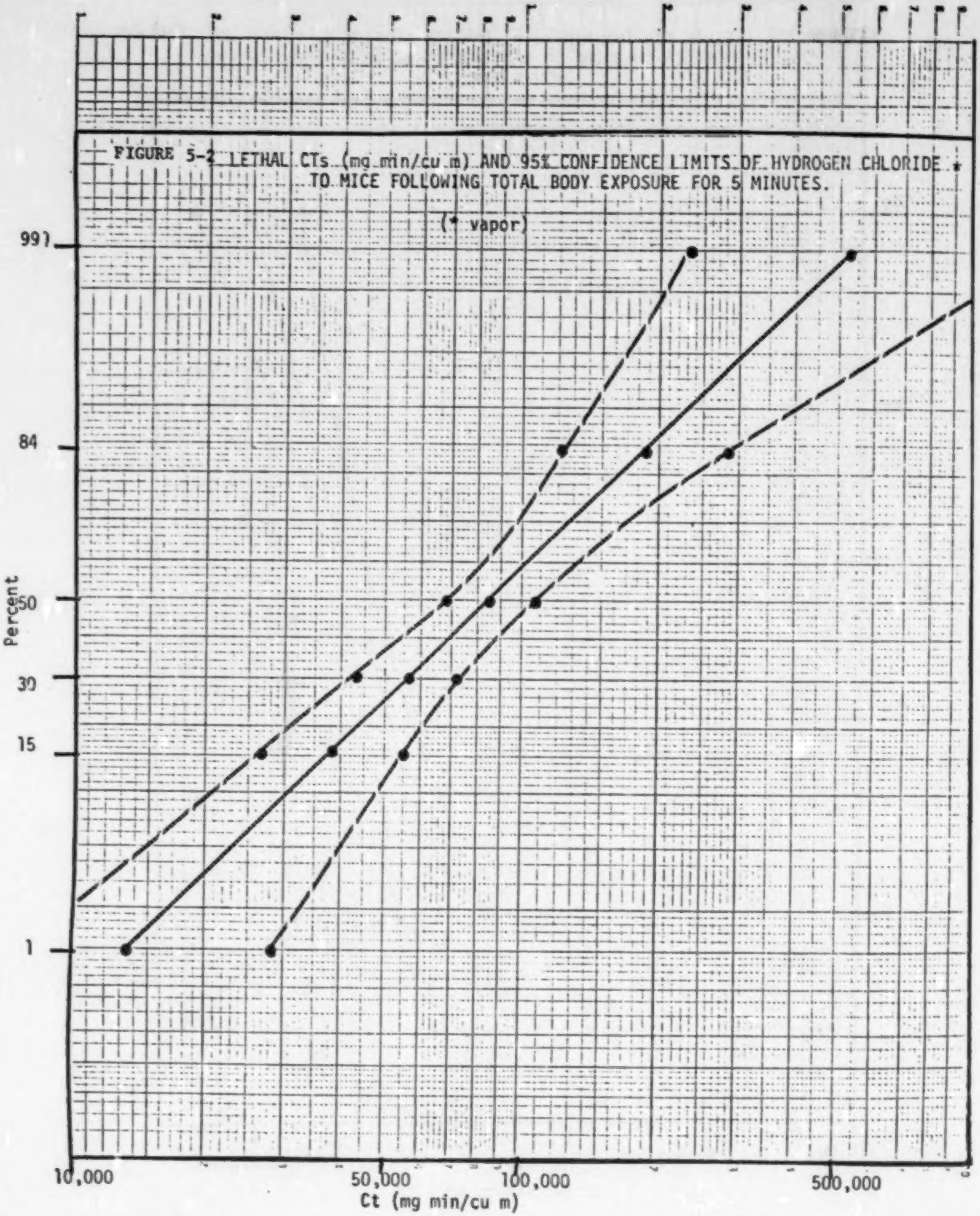
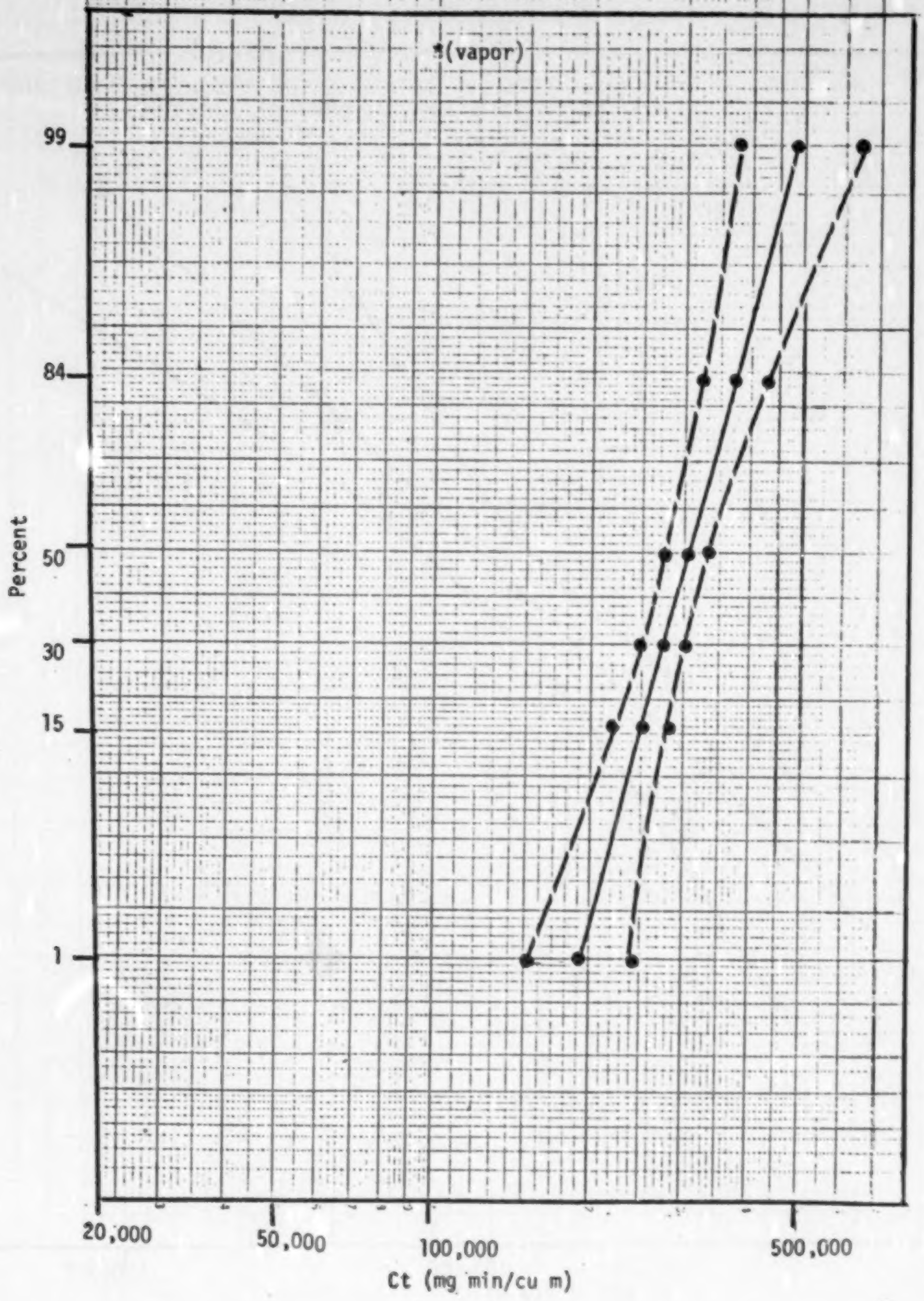


FIGURE 5-2 LETHAL CTs (mg min/cu m) AND 95% CONFIDENCE LIMITS OF HYDROGEN CHLORIDE * TO MICE FOLLOWING TOTAL BODY EXPOSURE FOR 5 MINUTES.

(* vapor)

FIGURE 5-3 LETHAL CTs (mg min/cu m) AND 95% CONFIDENCE LIMITS OF HYDROGEN CHLORIDE TO RATS FOLLOWING TOTAL BODY EXPOSURE FOR 5 MINUTES.



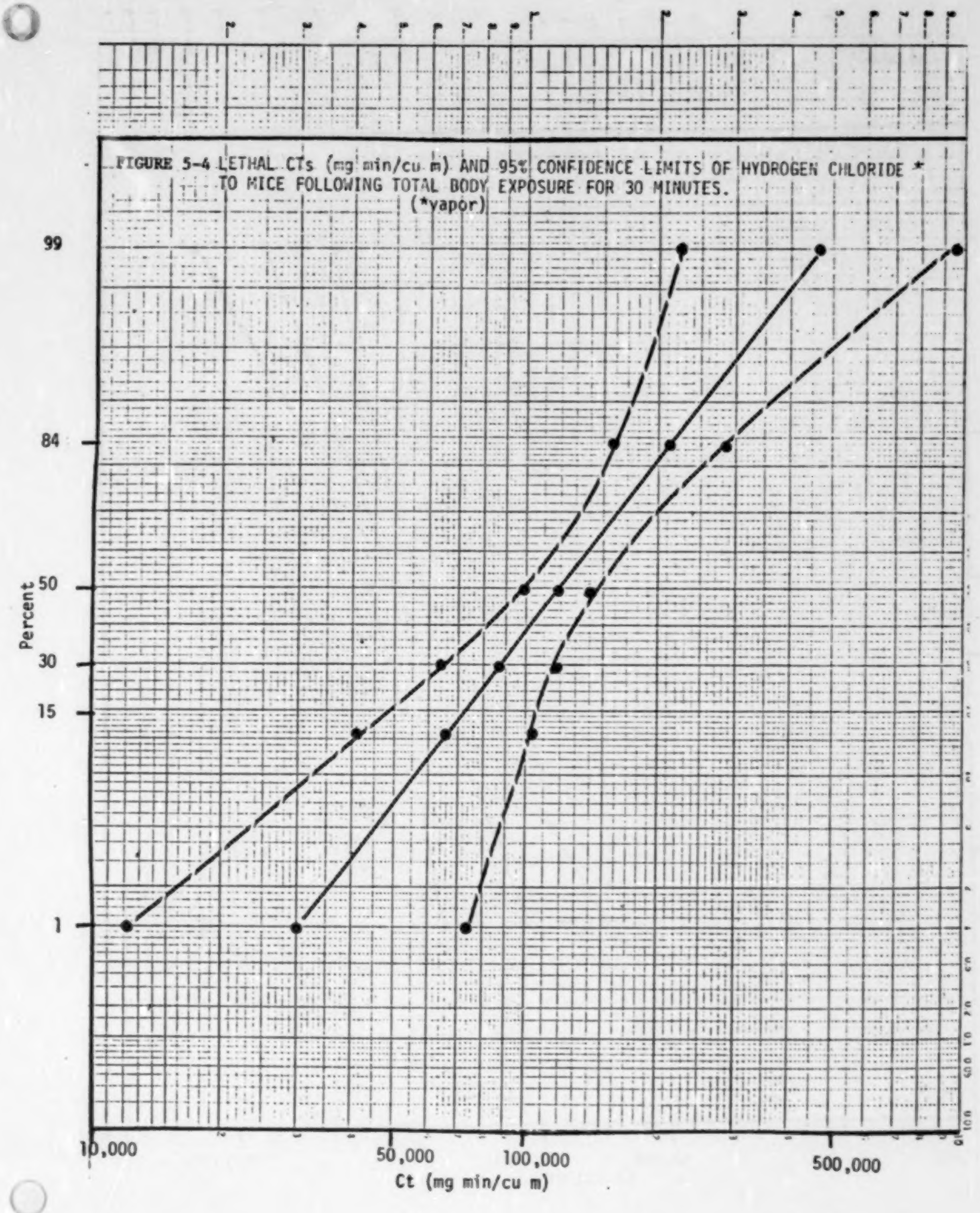
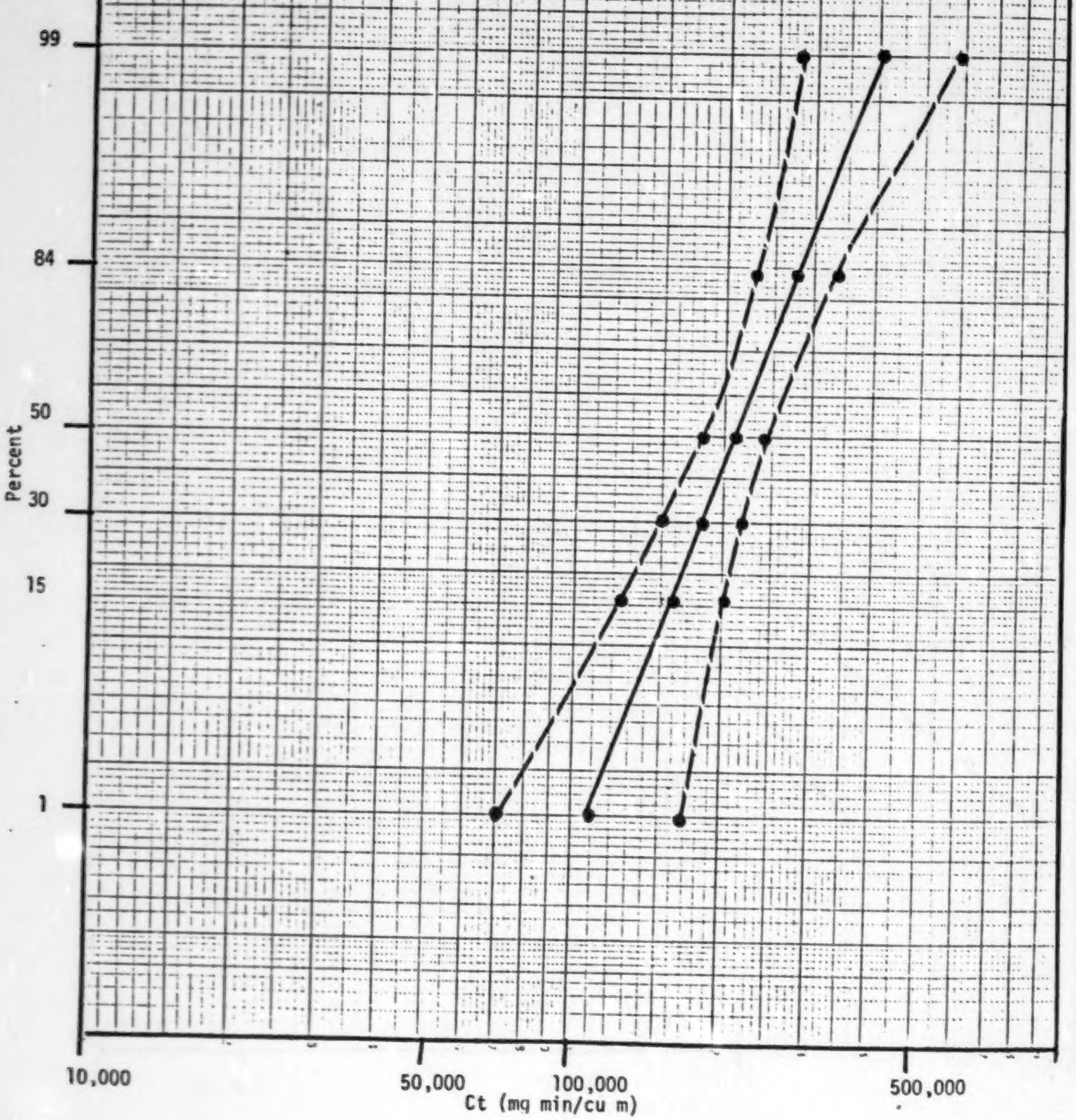


FIGURE 5-4 LETHAL CTs (mg min/cu m) AND 95% CONFIDENCE LIMITS OF HYDROGEN CHLORIDE * TO MICE FOLLOWING TOTAL BODY EXPOSURE FOR 30 MINUTES.
(*vapor)

FIGURE 5-5

LETHAL Cts (mg min/cu m) AND 95% CONFIDENCE LIMITS OF HYDROGEN CHLORIDE VAPOR TO RATS FOLLOWING TOTAL BODY EXPOSURE FOR 30 MINUTES



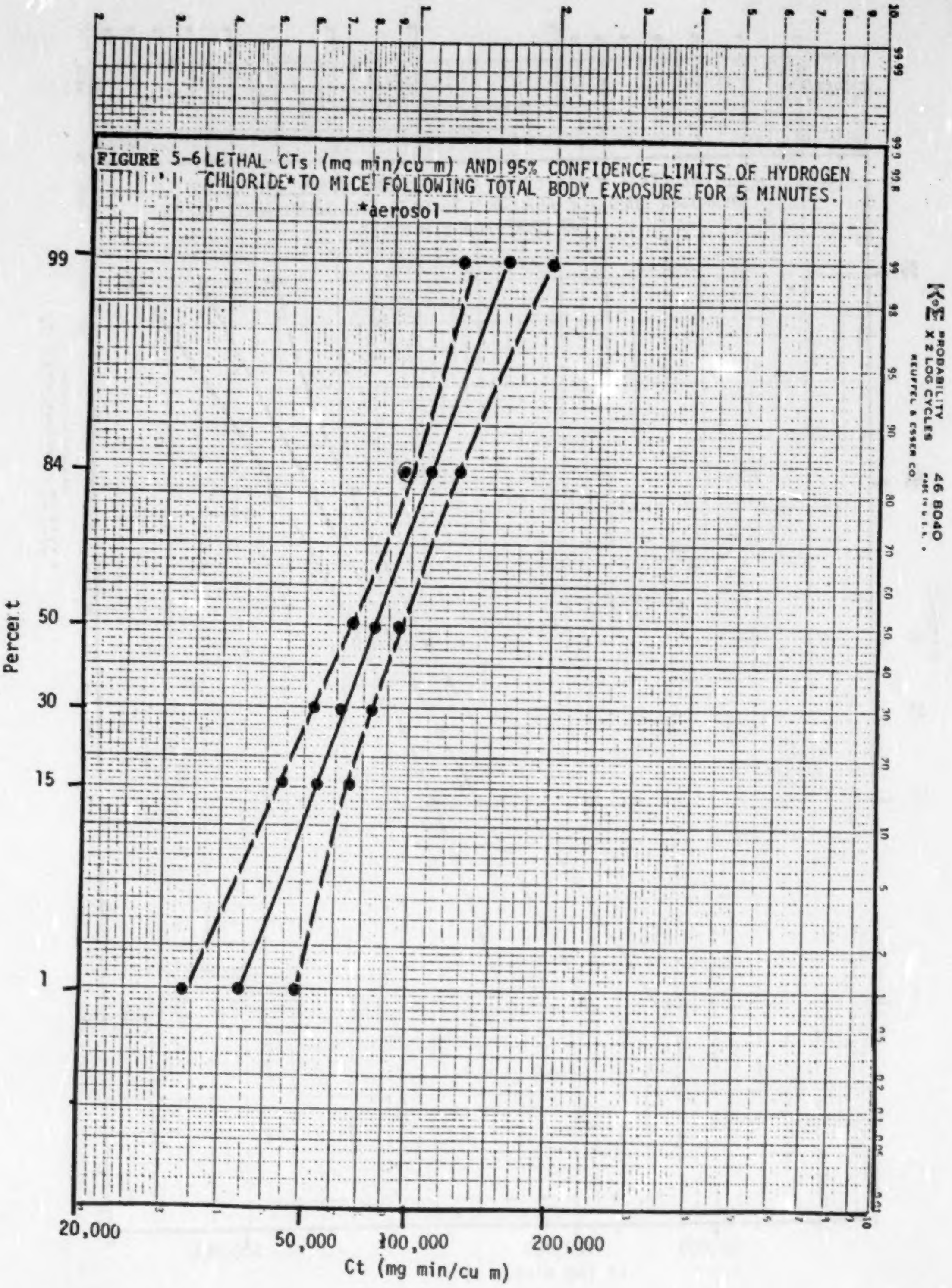


FIGURE 5-6 LETHAL CTs (mg min/cu m) AND 95% CONFIDENCE LIMITS OF HYDROGEN CHLORIDE* TO MICE FOLLOWING TOTAL BODY EXPOSURE FOR 5 MINUTES.

*aerosol

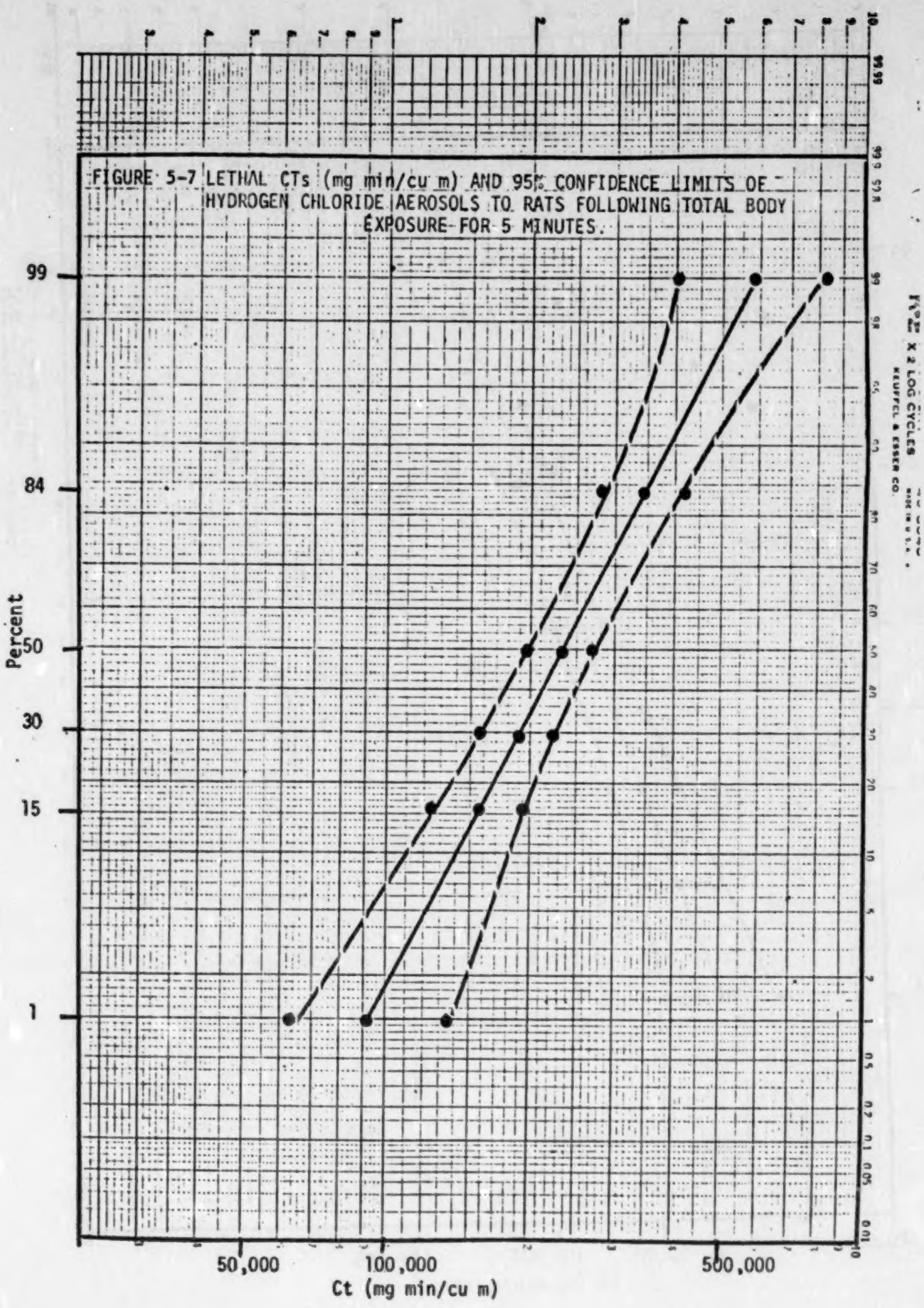


FIGURE 5-7 LETHAL CTs (mg min/cu m) AND 95% CONFIDENCE LIMITS OF HYDROGEN CHLORIDE AEROSOLS TO RATS FOLLOWING TOTAL BODY EXPOSURE FOR 5 MINUTES.

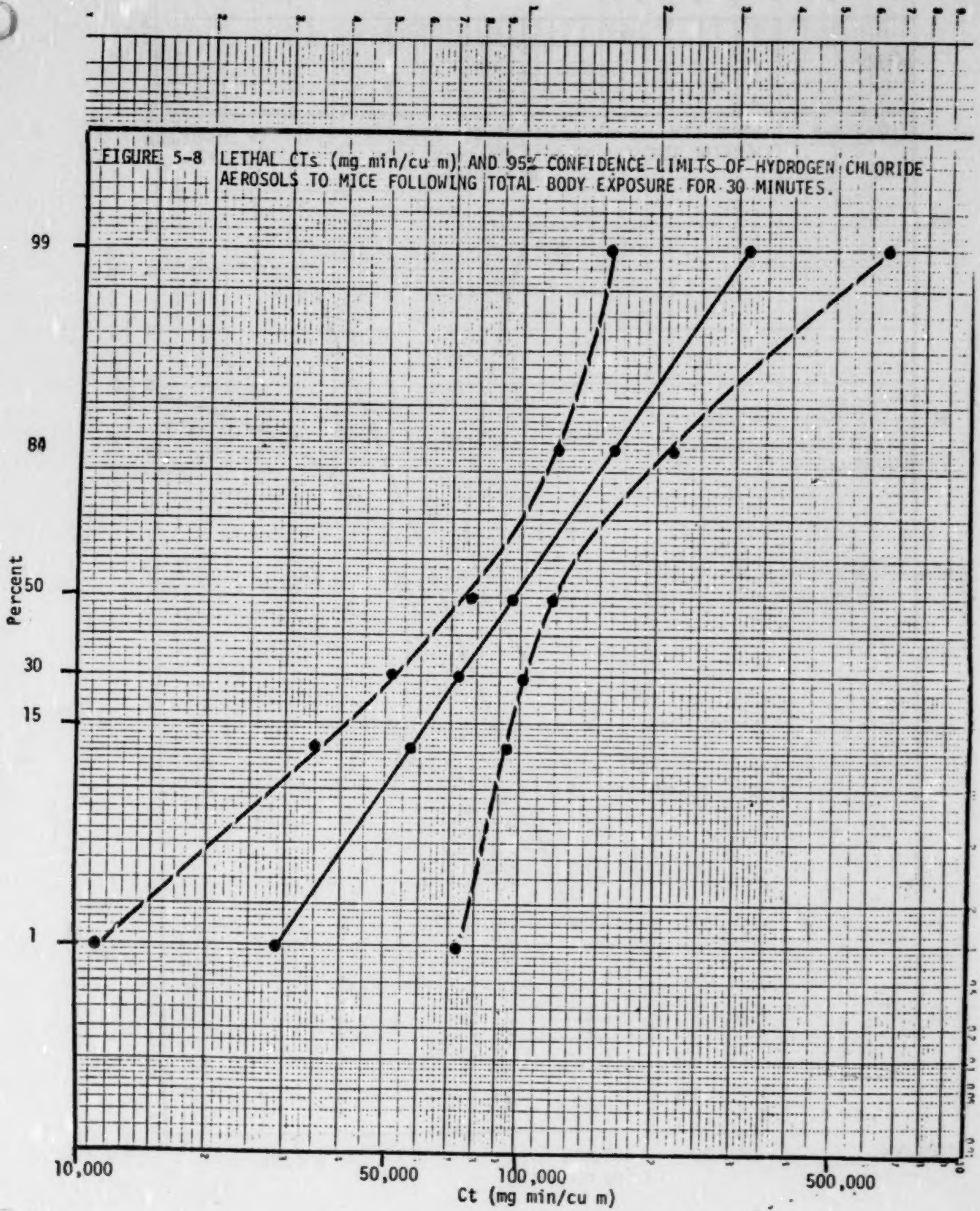


FIGURE 5-8 LETHAL CTs (mg min/cu m) AND 95% CONFIDENCE LIMITS OF HYDROGEN CHLORIDE AEROSOLS TO MICE FOLLOWING TOTAL BODY EXPOSURE FOR 30 MINUTES.

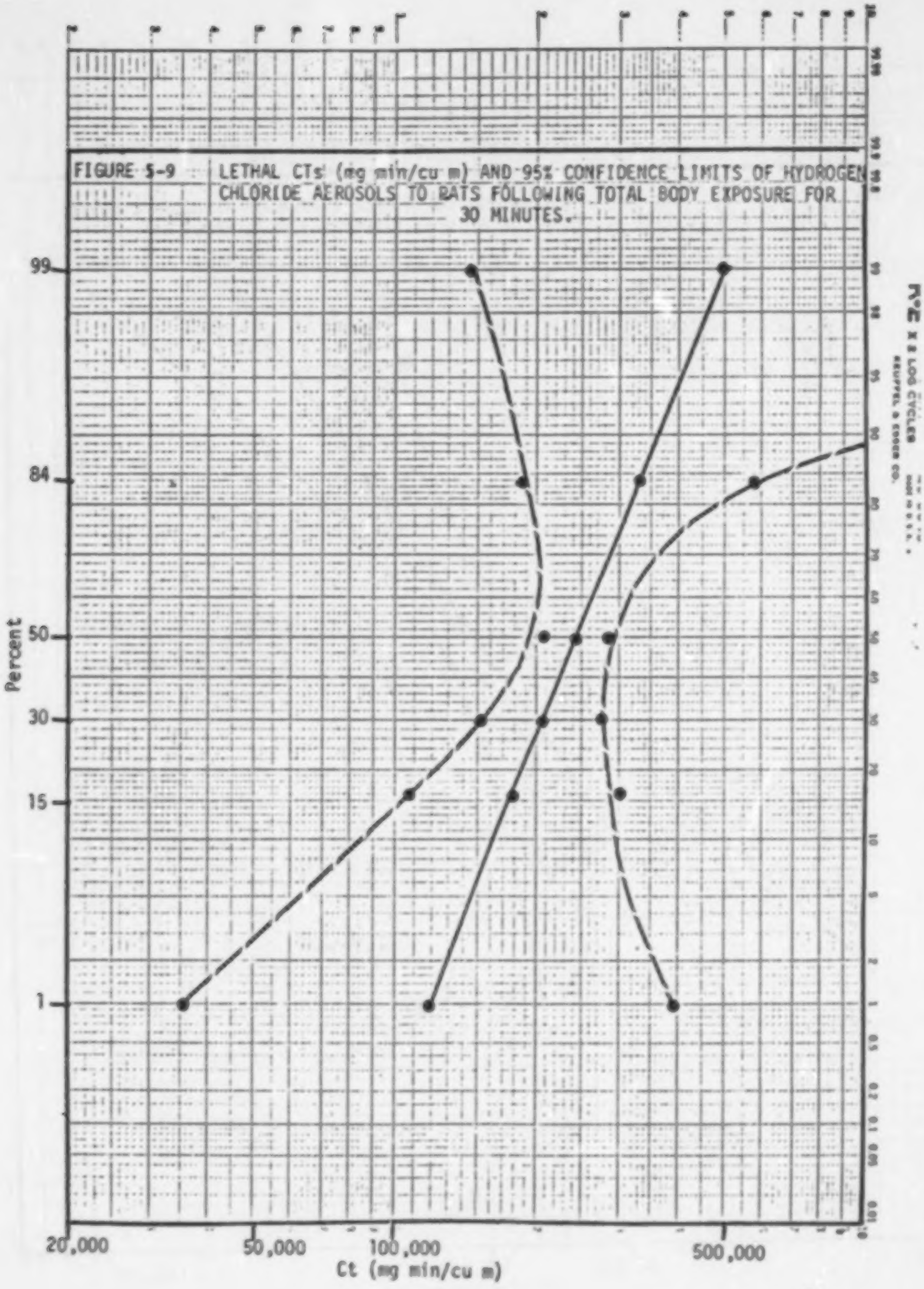


FIGURE 5-9 LETHAL CTs (mg min/cu m) AND 95% CONFIDENCE LIMITS OF HYDROGEN CHLORIDE AEROSOLS TO RATS FOLLOWING TOTAL BODY EXPOSURE FOR 30 MINUTES.

Mucociliary activity of excised rabbit trachea ceased permanently after exposed to hydrogen chloride vapor at 600 mg/m^3 (400 ppm) for 0.5 min, at 90 mg/m^3 (60 ppm) for 5 min, and at 45 mg/m^3 (30 ppm) for 10 min.[93]

Table 5-18 summarizes the available toxicity data on hydrogen chloride.

Repeated Exposures to Hydrogen Chloride Vapor

Machle *et al.*[315] exposed animals to hydrogen chloride gas at 0.05-20.5 mg/liter for periods of 5, 15, 60, 120, 360, 720, 1,800, or 7,200 min. One to six concentrations were used for each period. The exposures of 720 and 1,800 min were carried out 6 hr/day for 2 and 5 consecutive days, respectively. The 7,200-min exposure was carried out 6 hr/day for 5 days/week for 4 weeks. In each of 31 experiments, three rabbits and three guinea pigs were exposed; in the 7,200-min experiment, an adult female monkey was also used. The results of these tests are shown in Table 5-19. Deaths in the guinea pigs were attributed to acute respiratory damage. High concentrations caused necrosis of the trachea and bronchi, edema, atelectasis, emphysema, and damage to pulmonary blood vessels. Gross pathologic changes were noted in the livers of 45 of 57 guinea pigs that died, and pulmonary lesions were noted in guinea pigs that died or were sacrificed between 1-18 months after exposure. The rabbits were more resistant to the immediate effects of hydrogen chloride, but died later from pulmonary or nasal infections. Severe lesions were noted in the livers of 16 of 51 rabbits that died.

Ronzani[148] noted only slight unrest of the animals and irritation of the eyes and nose in rabbits, guinea pigs, and pigeons exposed to hydrogen chloride at 150 mg/m^3 (100 ppm) for 6 hr/day for 50 days. The hemoglobin concentration was only slightly diminished. Table 5-20 summarizes the available toxicity data on repeated exposures to hydrogen chloride vapors.

Table 5-21 shows a gradation of Ct's with corresponding toxicologic effects.

TABLE 5-18

Summary of Toxicity of Single Exposures of Animals to Hydrogen Chloride Vapor

Animals	Hydrogen Chloride Concentration. mg/m^3 (ppm)	Exposure Time, min	Ct, mg-min/m^3	Effect	Reference
Rabbits and guinea pigs	5,000 (3,400)	90	450,000	Deaths	148
	1,000 (650)	360	360,000	100% deaths	315
	6,500 (4,350)	30	195,000	100% deaths	315
	450 (300)	360	162,000	Cloudy cornea	148
	2,000 (1,350)	75	150,000	Respiratory distress	148
	5,500 (3,700)	5	27,500	No deaths	315
Cats and rabbits	150-210 (100-140)	Up to 360	<75,600	Running nose, salivation	148
Rats	60,000 (40,898)	5	300,000	LCt_{50}	101
	6,900 (4,701)	30	207,000	LCt_{50}	101
	47,500 (32,255)	5	237,500	Lowest dose causing death	101
	4,250 (2,910)	30	127,500	Lowest dose causing death	101
Mice	3,870 (2,644)	30	116,100	LCt_{50}	101
	20,200 (13,750)	5	101,000	LCt_{50}	101
	1,760 (1,204)	30	52,800	Lowest dose causing death	101
	4,750 (3,200)	5	23,750	Lowest dose causing death	101

TABLE 5-19

Toxicity of Hydrogen Chloride Gas in Animals[a]

No. Rabbits	No. Guinea Pigs	Hydrogen Chloride Concentration, mg/m^3 (ppm)	Exposure Time, min	Results
3	3	6,500 (4,350)	30	100% deaths
3	3	1,000 (650)	360	100% deaths
3	3	5,500 (3,700)	5	No deaths
3	3	100 (65)	1,800	b
3	3	50 (33)	7,200	No effects, no pathologic changes

---

[a] Data from Machle *et al.*[315]

[b] Mild inflammatory reactions in bronchi, with peribronchial fibrosis and lymph node hyperplasia, in guinea pigs; lobular pneumonia and pulmonary abscesses in rabbits.

TABLE 5-20

Summary of Repeated Exposures of Animals to Hydrogen Chloride Vapor

Animals	Hydrogen Chloride Concentration mg/m^3 (ppm)	Exposure Time, min	Daily Ct, mg-min/m^3	Effect	Reference
Rabbits guinea pigs	100 (65)	1,800[a]	36,000	Inflammatory reaction in respiratory tract	315
Rabbits, guinea pigs, and monkeys	50 (33)	7,200[b]	18,000	No effects, no pathology	315
Rabbits guinea pigs, and pigeons	150 (100)	18,000[c]	54,000	Unrest, irritation of eyes and nose	148

---

[a] 360 min/day for 5 days.

[b] 360 min/day for 20 days.

[c] 360 min/day for 50 days.

TABLE 5-21

Ct's and Effects Produced by Hydrogen Chloride Vapor in Animals

Effect	Ct, mg-min/m^3
Lethal to 100%	200,000 - 450,000
Lethal to 50%	100,000 - 300,000
Cloudy corneas, catarrh	150,000
Irritation, rhinorrhea, salivation	50,000
Rare deaths or pathology	<10,000

Tables 5-18 and 5-20 indicate that mice are more sensitive to the lethal effects of hydrogen chloride vapor than rats, guinea pigs, rabbits, or monkeys. Also, within a given species, the degree of damage produced by hydrogen chloride is related to the Ct over the known ranges of concentration and exposure. The LCt_{50} for mice is about half that for rats.

It is indicated also that irreversible toxic effects or death would occur only rarely after single exposures of 5 min or more at a Ct of 10,000 mg-min/m^3 or less, even in mice. The LCt_{50} is about 100,000 mg-min/m^3 for mice and about 250,000 mg-min/m^3 for rats when the exposure time is 5 or 30 min. At the LCt_{50} clouding of the cornea occurs in rabbits and guinea pigs. The studies of Lehmann[148] and of Ronzani[148] in rabbits and guinea pigs indicate that irritation, salivation, and rhinorrhea occur at a Ct of about 50,000 mg-min/m^3.

The studies show that, in rabbits, guinea pigs, and monkeys, daily Ct's of 18,000 mg-min/m^3 (50 mg/m^3 for 6 hr/day) for 20 days do not cause any signs of irritation or morphology.

Except for the effects on the eyes, skin, and respiratory tract, the single mention of hemoglobin, and the liver pathology, there is little published information on the effects of inhaled hydrogen chloride on the various body organs or systems.

Intrabronchial Insufflation of Hydrochloric Acid

Winternitz *et al.*[519] insufflated 5 ml of 0.1-1% hydrochloric acid in saline into the lungs of anesthetized rabbits. The 1% solution caused death within 3-5 min. The lungs filled the pleural cavities. The pleural surfaces were tense and often hemorrhagic. When sectioned, the lungs contained large quantities of blood-stained fluid. The tracheas and larger parts of the bronchi contained blood-stained fluid and hemorrhaged into the mucosa.

The 0.25% solution seldom produced sudden death. Most of the animals came out of anesthesia and later showed no untoward symptoms, except pulmonary infection. Animals sacrificed at intervals after insufflation showed destruction of the epithelium of the bronchioles, the alveolar ducts, and the alveoli. There was exudation into the alveolar, interstitial perivascular, and peribronchial tissues. In some areas, there was consolidation, with or without destruction in the alveolar walls. Later, there was organization of the exudate, necrosis, and proliferation of the epithelium and bronchi. Pulmonary parenchyma finally regenerated.

Other investigators have reported the effects of intratracheal administration of hydrochloric acid solutions in rabbits,[181] dogs,[64,183] and cats.[302,503] Positive-pressure ventilation was considered an aid to survival in rabbits and dogs.[64,181,183] Ventilation with oxygen immediately after exposure to the acid was said to spread the damage and to increase mortality in cats.[503]

EFFECTS OF HYDROGEN CHLORIDE ON MAN

Compared with chlorine, there is a paucity of data available on the human effects of exposure to gaseous hydrogen chloride. Aside from the studies of Toyama et al.[481] in 1962, ten Bruggen Cate[469] in 1968, and Leondardos et al.[299] in 1969 and the subjective-response data of industrial hygienists in 1973, most of the material in western literature is derived from much older studies.

The Russians have reported on experimental work with human volunteers. This work includes not only data on the physiologic response of odor, as recognized in the United States, but also "odor" or reflex effects as determined by changes in optical chronaxy, eye adaptation to darkness, respiratory rhythm, or other test techniques not commonly used by experimenters in other scientific communities. Rjazanov,[395] in an article in 1965, discussed the U.S.S.R. Criteria and Methods for Establishing Maximum Permissible Concentrations of Air Pollution.

In both anhydrous and aerosol forms, hydrogen chloride is a strong irritant, affecting the conjunctiva and the mucous membranes of the respiratory tract. Because of its solubility in water, the major effects of acute exposure are usually limited to the upper passages of the respiratory system and are of sufficient intensity to encourage prompt voluntary withdrawal from a contaminated atmosphere. The warning properties are such that acute exposure causing significant trauma is limited to people who are prevented from escaping. In man, the effects are usually confined to inflammation and possibly ulceration of the nose, throat, and larynx.[322] However, on rare occasions, laryngeal spasm or pulmonary edema may occur.[411]

According to Heyroth,[207] most people can detect 1-5 ppm, with 5-10 ppm being disagreeable. He also noted, however, that others have stated that up to 35 ppm cannot be detected by either odor or taste.

Leonardos et al.[74] determined experimentally that the odor threshold concentration of hydrogen chloride was 10 ppm.

Hoyle (personal communication), in rating subjective responses of trained industrial hygienists, reported that no response was observed at 0.06-1.8 ppm, minimal response was noted at 0.07-2.17 ppm, the material was easily noticed at 1.9-8.6 ppm, and a strong response was obvious at 5.6-22.1 ppm (Table 5-22).

Matt[148] reported that work was undisturbed at 10 ppm, difficult at 10-50 ppm, and impossible above 50 ppm.

However, Sax[411] said that, although short exposures to 35 ppm could cause irritation of the throat, work was possible at 50-100 ppm for an hour. He noted that severe exposure could cause pulmonary edema or laryngeal spasm, with 1,000-2,000 ppm for brief periods being dangerous.

TABLE 5-22

Subjective Response to Hydrogen Chloride[a]

Response	No. Observations	Hydrogen Chloride Concentration, ppm	
		Average	Range
None	6	0.4	0.06 - 1.8
Minimal	4	0.7	0.07 - 2.17
Easily noticed	5	4.17	1.9 - 8.6
Strong	5	13.37	5.6 -22.1

---

[a] Data from H. R. Hoyle (personal communication).

In the Russian literature, Melekhina[340] reported the odor threshold at 0.39 mg/m^3 (0.26 ppm). Styazhkin[456] stated that the odor threshold was 0.2 mg/m^3 (0.13 ppm), and Elfimova,[126] 0.1 mg/m^3 (0.067 ppm).

Eye and skin burns have been observed at higher concentrations. However, it has been reported that flushing with copious amounts of water will prevent most of the serious damage.[322] This was confirmed by Nagao *et al.*[353] in 1972. They reported that, after application of 1N hydrochloric acid solution, the first damage to the living cells of the skin was not noted microscopically before 120 min. If the acidic solution remains in contact with the tissues for relatively long periods, damage can occur. For example, it is possible that enough gaseous hydrogen chloride will go into solution in perspiration-soaked clothes to cause dermatitis.[322]

Ten Bruggen Cate,[469] in 1968, published a report on dental erosion associated with exposures to various mineral acids, including hydrochloric acid. In most of the exposures, hydrochloric acid was in combination with other acids, primarily sulfuric. The pathologic effects observed were etching and erosion of the front teeth. However, there was no apparent increase in dental caries. There was some correlation of severity of pathology with degree and duration of exposure.

Aside from dental erosion, no significant abnormalities have been associated with chronic exposuresto low concentrations of gaseous hydrogen chloride. Toyama *et al.*[481] noted that workers chronically exposed did not exhibit the pulmonary-function changes observed in people acutely exposed to similar concentrations; this suggests acclimation.

Table 5-23 summarizes the reported effects of hydrogen chloride on man.

TABLE 5-23

Summary of Human Effects of Exposure to Hydrogen Chloride

Hydrogen Chloride Concentration, ppm	Exposure Time	Effects or Comments	Reference
1,300-2,000	Few minutes	Lethal	241, 449a
1,000-1,300	30-60 min	Dangerous	241
1,000-2,000	--	Brief exposures dangerous	411
50-100	--	Work impossible	207, 148
50-100	60 min	Intolerable	411, 148, 202, 241
35	--	Irritation of throat after short exposure	411
10-50	--	Work difficult but possible	207, 148
35	--	Undetectable by odor or taste in some	207
10	--	Irritation	450
10	--	Work undisturbed	207, 148
10	--	Odor threshold concentration	299, 451
5	--	No organic damage	450
1-5	--	Odor threshold concentration	207
0.402	--	Optical chronaxy reflex threshold concentration	322
0.335	--	Digitovascular toxicity threshold concentration	126
0.26	--	Odor threshold concentration	340
0.134	--	Threshold concentration for reflex effect on eye sensitivity to light	127, 126
0.13	--	Odor threshold concentration	456, 126

TABLE 5-23 - continued

Hydrogen Chloride Concentration, ppm	Exposure Time	Effects or Comments	Reference
0.067-0.134	--	Odor threshold concentration	127, 126
0.067-0.134	--	Threshold concentration for change in rhythm and depth of respiratory movement	127, 126
--	3 mo	Earliest etching of tooth enamel in plant workers	469
--	18 mo	Earliest erosion of tooth enamel in plant workers	469
--	6 yr	Earliest erosion to expose secondary dentin in plant workers	469

Mutagenesis, Teratogenesis, and Carcinogenesis

No mutagenic, teratogenic, or carcinogenic effects of exposure of humans to gaseous hydrogen chloride have been reported.

Recent data indicate that gaseous hydrogen chloride and formaldehyde can react in the atmosphere to form bis-chloromethylether, a reported carcinogen. This reaction does not occur at concentrations of hydrogen chloride or formaldehyde at or below the current threshold limit value.[43,143,359]

Combined Exposures to Hydrogen Chloride and Other Irritants

Styazhkin[457] determined experimentally the odor threshold concentrations of hydrogen chloride gas and chlorine simultaneously present in atmospheric air. He determined the odor threshold concentrations first for each chemical individually and then for various combinations. Expressing each chemical as a fraction, determined by the experimental dose relative to the odor threshold concentrations, he found that, when the sum was unity or more, the odor of the combination was perceptible. To express this in another way, when X in the following formula is equal to or greater than 1, odor is perceptible:

$$X = \frac{\text{concentration of } Cl_2}{\text{odor Threshold of } Cl_2} + \frac{\text{concentration of HCl}}{\text{odor Threshold of HCl}}.$$

Melekhina[340] studied the threshold concentrations of combinations of three mineral acids. Using various concentrations of gaseous sulfuric, nitric, and hydrochloric acids, he also found that the determination of odor threshold concentration involved arithmetic summation.

Established Limits

Air quality standards for hydrogen chloride are summarized in Table 5-24, and Table 5-25 presents short-term and emergency limits for man.

TABLE 5-24

Environmental Air Standards for Hydrogen Chloride

Hydrogen Chloride Concentration, mg/m^3 (ppm)	Source
7 (5)	TLV, ACGIH[8a]
-- (5)	West Germany, permissible work-station concentration[267]
0.7 (0.5)	30-min mean average with maximum of 1.0 ppm[267]
0.015 (0.009)	Russian 24-hr maximal average[267,328]
0.05 (0.03)	Maximum for single exposure[267,328]
-- (0.02)	Czechoslovakian 24-hr maximal mean[405]
-- (0.07)	Maximal single exposure[405]

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[a] Adopted by Occupational Safety and Health Administration.[489]

TABLE 5-25

Short-Term and Emergency Limits for Public Exposure to Hydrogen Chloride[a]

Duration	Hydrogen Chloride Concentration, mg/m^3 (ppm)
Short-Term Public Exposure Limits:	
10 min	6 (4)
30 min	3 (2)
60 min	3 (2)
1 hr/day	3 (2)
5 hr/day, 3-4 days/mo	1 (0.7)
Public Emergency Limits:	
10 min	10 (7)
30 min	5 (3)
60 min	5 (3)

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[a] Derived from National Research Council Committee on Toxicology.[356]

CHAPTER 6

EFFECTS OF CHLORINE AND HYDROGEN CHLORIDE ON VEGETATION

EFFECTS OF CHLORINE ON VEGETATION

Damage to vegetation due to chlorine gas was reported to have occurred at least 100 years ago in Europe, near brickworks, clay product plants, and chemical plants. In recent years, damage to vegetation from this gas has usually been the result of accidental leakage, breaks in a line, etc. Zimmerman[531] reported two cases of accidental damage to vegetation near Yonkers, N.Y. One case resulted from the escape of gas from a cylinder at a swimming pool, and the other, from an accidental leak at a factory. About 30 species of plants were injured in these two cases, including tree of heaven, apple, cherry, maple, smartweed, basswood, dogwood, elm, ash, sweetgum, hemlock, oak, and white pine.* Stout[454] reported chlorine injury to lettuce and weeds growing near a sewer plant whose chlorinating apparatus leaked. The concentrations of chlorine in the ambient air as a result of these accidents are not known. However, the phytotoxic potential of chlorine has been determined by fumigation under controlled conditions.

Haselhoff and Lindau[195] summarized the literature on chlorine and hydrochloric acid in 1903 and reported that Turner and Christison were probably the first to have investigated experimentally the injurious action of chlorine and hydrochloric acid on vegetation. According to Turner and Christison, an exposure to 2 ml of chlorine in 200 ml of air for 3 hr was the threshold dose needed to cause injury on mignonette. Haselhoff and Lindau also summarized the work of Richardson, who exposed spruce, pine, cactus, myrtle, and mignonette to chlorine gas diluted to

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*Common and scientific names of plants are listed in the appendix to this chapter.

1:5,000 for 12 hr. The leaves dried up, shriveled, yellowed, and died. These early results were obtained without adequate air circulation over the plants, so the stated concentrations should not be taken as representative of actual outdoor fumigation.

In 1934, Weiler[509] described chlorine injury to sugar beets and red clover. The injury was characterized as white spots on sugar beets and brown spots on the clover leaves. Weiler believed that the gas had entered the leaf via the stomata on the upper side of the leaf, because the dead cells were found in the vicinity of these stomata and extending downward into the mesophyll. Cells adjacent to the necrotic tissue had thickened walls. A strong layer of cork formed in the mesophyll below the damaged area. In clover, the injury extended down into two or three layers of palisade parenchyma.

McCallan and Setterstrom,[332] McCallan and Weedon,[333] Thornton and Setterstrom,[477] and Barton[18] undertook an extensive cooperative project to determine the comparative toxicity of ammonia, chlorine, hydrogen cyanide, hydrogen sulfide, and sulfur dioxide gases to 18 species, including fungal and bacterial plant and animal pathogens, green leaves and stems, seeds, sclerotia, insects, and rodents. Their fumigation apparatus permitted a continuous flow of gases at controlled concentrations. The exposure concentrations ranged from 1 to 1,000 ppm for periods of 1-960 min. At 1,000 ppm, the orders of toxicity of gases were as follows: for fungi and bacteria--sulfur dioxide, chlorine, ammonia, hydrogen sulfide, hydrogen cyanide; for seeds and sclerotia--sulfur dioxide, chlorine, ammonia, hydrogen cyanide, hydrogen sulfide; for green leaves--chlorine, sulfur dioxide, ammonia, hydrogen cyanide, hydrogen sulfide; and for green stems--no difference. The plant pathogens included _Sclerotium delphinii_, _Rhizoctonia tuliparum_, _Botrytis_ sp., *Sclerotinia fructicola*, *Pestalotia stellata*, *Glomerella cingulata*, *Macrosporium sarcinaeforme*, and *Ceratostomella ulmi*. Sclerotia of the following plant pathogens were also fumigated: *Sclerotium delphinii*, *Botrytis* sp., and *Rhizoctonia tuliparum*. The seeds included soaked and dry rye and radish. The green stems and leaves included tomato, tobacco, and buckwheat. The order of sensitivity of classes of organism was as follows for chlorine: leaves, fungi and bacteria, stems, animals, seeds, and sclerotia. Young cultures and sclerotia were much more sensitive to chlorine than older ones. With all plant pathogens and all gases, there was a conspicuous delay in the visible growth of viable cultures after transfer to fresh media.

Acute Injury

Thornton and Setterstrom[477] reported that chlorine injury is manifested by a discoloration of the leaf, which eventually turns brown. With tomato, buckwheat, and tobacco, chlorine at 0.46-2.95 ppm for 20-480 min caused injury to the older leaves in the form of interveinal chlorosis, which was followed by a bleaching and breakdown of the entire leaf tissue.

Benedict and Breen[30] fumigated 10 weed species to chlorine at a high (2.5 ppm) and a low (0.5 ppm) concentration. The fumigations were run from approximately 10:00 a.m. to 2:00 p.m., to provide the maximal amount of sunlight, so that the plant stomata would be open, thereby ensuring optimal conditions for marking. The following plants were fumigated: annual bluegrass, cheeseweed, chickweed, dandelion, Kentucky bluegrass, lamb's quarter, mustard, nettle-leaf goosefoot, pigweed, and sunflower. Necrotic areas were produced between the veins on the broad-leaved plants, but they usually developed close to the margin and with increased intensity of fumigation spread toward the midrib.

With the grasses, the markings first appeared as marginal streaks progressing toward the main vein, in the region between the tip and the point where the grass leaf bends over. The markings usually occurred alongside the veins. Middle-aged and older leaves were about equally marked with necrotic areas and were usually marked more severely than new leaves. White to tan markings were produced on mustard, annual and Kentucky bluegrass, chickweed, nettle-leaf goosefoot, and lamb's quarter. Chlorine sometimes produced an overall bleaching of the leaf without killing the tissue. The color was generally light green, with some yellow occasionally.

Zimmerman[531] fumigated 19 species of plants with chlorine at 0.46-4.67 ppm and found 16 were susceptible to injury at those concentrations. Of the susceptible species, those of most interest were peach, coleus, cosmos, buckwheat, and hybrid tea. Chinese holly, eggplant, and tobacco had no visible injury from any of the treatments. He stated that the most characteristic response of the various species was spotting of the leaves similar to the effects of sulfur dioxide. The spots appear first as cooked areas, but turn straw-colored or brown after a few days. Threshold concentrations for acute injury were reported to be 0.46 ppm for 1 hr for buckwheat, 0.56 ppm for 2 hr for coleus, 0.56 ppm for 3 hr for peach, 0.56 ppm for 2 hr for silverbell-tree, 1.3 ppm for 2 hr for bramble, 1.3 ppm for 0.5 hr for bean and radish, and 1.5 ppm for 0.5 hr for rose. Threshold concentrations and times were not given for cosmos and hybrid tea.

Brennan _et al_.[51] fumigated plants with chlorine at 0.10-1.50 ppm for 4 hr. They reported considerable variation in the symptoms produced, depending on the species and the concentration of the gas. At high concentration, water-soaking of the foliage and often wilting could be observed by the end of the fumigation period. Within a day or so fumigation, necrosis and bleaching of the leaves developed. A marginal necrosis developed in alfalfa and begonia, and scattered necrotic areas developed on leaves of tomato, tobacco, and radish. In general, the necrotic areas appeared between the veins, but there were exceptions. In monocots, the necrotic areas were produced between the veins, giving the appearance of streaks. In onion and pine, the necrosis appeared at the tip and extended downward, as the exposure increased. The markings on the affected tissue varied from almost white or tan to brown. Orange-brown necrotic areas developed consistently in some species, such as apple, pine, and maple. At low exposure, the typical response observed was a bleaching of the foliage.

Brennan et al.[52] fumigated three species of pine with chlorine (shortleaf, slash, and loblolly). The needles of all three species were visibly injured by a 3-hr fumigation at 1.00 ppm.

Chronic Injury

Although chronic fumigations have apparently not been run for chlorine, it is logical to assume that chronic injury would result if the concentration of the gas were low enough during the fumigation. Brennan et al.[51] reported that epinasty often occurred after fumigation that was insufficient to mark tomato foliage. Leaf cupping was sometimes produced on squash. In Chenopodium, there was a tendency for leaves to abscise after fumigation.

Metabolic Effects

There are no reports in the literature on the metabolic effects of chlorine gas on vegetation.

Sensitivity

Benedict and Breen[30] reported that, of 10 weed species fumigated, mustard, chickweed, and sunflower were the most sensitive; dandelion, cheeseweed, nettle-leaf goosefoot, and annual bluegrass were intermediate in sensitivity; and Kentucky bluegrass, lamb's quarter, and pigweed were the most resistant. Brennan _et_ _al_.[52] have reported that shortleaf, slash, and loblolly pines are considerably more resistant to chlorine gas than many herbaceous species. The threshold concentration for injury appears to be 1 ppm for a 3-hr exposure. The results of work by a number of investigators with respect to sensitivity of plants to chlorine gas are summarized in Table 6-1.

Benedict and Breen[30] reported that plants under low soil-moisture conditions were marked less than those grown under high soil-moisture conditions. The age of their weeds also seemed to be important in affecting this sensitivity; the 6-week-old plants were more sensitive than the 3-week-old plants. The age factor was confounded by soil-moisture stress, inasmuch as the 3-week-old plants and the 6-week-old plants on dry soil were about equally marked by the high and low concentrations of chlorine, but the 6-week-old moist-soil plants were more severely marked at high concentration.

Brennan _et_ _al_.[51] reported that the presence of moisture on the leaves of plants did not seem to affect their sensitivity to chlorine. They also reported that shade (darkness) has a tendency to minimize damage, if the shade period follows fumigation. If the shade period precedes fumigation, there is no effect. Water stress, as well as closing of the stomata by artificial means, has a tendency to reduce the sensitivity of tomato to chlorine gas. Zimmerman[531] also reported that water stress, even slight wilting, causes plants to become resistant.

TABLE 6-1

Relative Sensitivity of Plants to Chlorine Gas[a]

Sensitivity	Intermediate	Resistant
Alfalfa	Annual bluegrass	Azalea
Blackberry	Buckwheat	Balsam fir
Box elder	Cheeseweed	Begonia
Chickweed	Corn	Cactus
Crab apple	Cucumber	Chrysanthemum
Globe-amaranth	Dahlia	Corn
Horse-chestnut	Dandelion	Cowpea
Mustard	Nasturtium	Geranium
Pin oak	Nettle-leaf goosefoot	Kentucky bluegrass
Radish	Onion	Lamb's quarter
Rose	Petunia	Mignonette
Sugar maple	Pinto bean	Myrtle
Sunflower	Scotia bean	Oxalis
Sweetgum	Squash	Pepper
Tobacco	Tomato	Pigweed
Tree of heaven		Pine
Tulip tree		Smartweed
Virginia creeper		
Wandering Jew		
Zinnia		

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[a] Data from Benedict and Breen[30] Brennan *et al.*,[51] Haselhoff and Lindau,[195] McCallan and Setterstrom,[332] Shriner,[426] and Thornton and Setterstrom.[477]

Brennan et al.[52] reported that pine trees in a hardened condition were less sensitive than those actively growing.

Accumulation of Chlorides

Brennan et al.[51] analyzed tomato foliage for chlorine immediately after fumigation at concentrations ranging from 0.40 ppm for 6 hr to 1.40 ppm for 3 hr. They found that the chloride content of the tissues was related neither to the degree of chlorine exposure nor to the amount of damage produced by the gas in these short-term fumigations. However, the chloride content of the petioles was considerably higher than that of any other tissue fraction in the plant. The concentration in the lower leaves was appreciably more than that in the top leaves. Exposure of the plants to an atmosphere of chlorine did not alter the pattern of chloride distribution within the plant, and there was no appreciable increase in the chloride content of any of the fractions after fumigation. They concluded that their evidence did not support chemical analysis for chloride as a method of diagnosing chlorine injury caused by air pollution. They also reported elsewhere[52] that the chloride content of pine needles generally increased after chlorine fumigation, but the increment was proportional neither to the degree of fumigation nor to the extent of damage.

Indirect Effects

Rjazonov[395] reported that Krasinskii had conducted studies to distinguish between the effects of chlorine on the soil, the root system, and the aboveground part of plants. Chlorine did not directly affect a plant's root system, because it almost immediately united with solid constituents to form chlorides. Chlorides are highly water-soluble, so they were easily washed out by subsoil water movements, thereby depriving the soil of its original fertility and particularly of its base elements.

Mimicking Symptoms

The general pattern of injury by chlorine is similar to that reported for injury of some species by ozone--for example, mustard, Italian prune, and ginkgo. Chlorine injury of some conifers, such as larch, causes a chlorotic needle mottle that looks very similar to oxidant-sulfur dioxide injury of white pine. Chlorine injury of white pine appears as a light to reddish-tan necrosis of the needle tips. Although the result is generally lighter than tip-burn caused by other pollutants, the injury could be confused with acute ozone or sulfur dioxide injury.

EFFECTS OF GASEOUS HYDROGEN CHLORIDE ON VEGETATION

The effects of hydrogen chloride gas on vegetation were first noted in Europe and Great Britain in the vicinity of alkali plants during the midnineteenth century. In the early days of the Le Blanc soda process, sodium chloride was treated with sulfuric acid, and hydrogen chloride gas was released as an unwanted byproduct. Extensive studies on the damaged vegetation were undertaken at that time by Haselhoff and Lindau.[195] Scrubbers installed at the various alkali works in England between 1836 and 1863 removed at least 95% of the hydrogen chloride in the stack gases. In 1874, the concentration in the stack gases was limited to 0.45 mg/m^3, and that in effect eliminated crop damage. After the passage of the Alkali Act of 1906 in Great Britian, there were no further reports of crop damage by this contaminant.

In 1934, Weiler[509] reported damage to plants by hydrochloric acid. The following plants were examined in more detail in the field: osier, white thorn, elm, linden, oak, lilac, cherry tree, plum tree, Virginia creeper, Oregon grape, dragon tree, strawberry, red currant, one species of Chenopodium, pine, and spruce. According to Weiler, the appearance of damage depended heavily on the nature of the carrier of the acid and on the species examined. Extensive damage in the form of dots or spots can be expected if the acid was carried by rain, dew, or fog. The most common type of damage was the peculiar ring formation on the leaves. This developed supposedly as a result of deposition of droplets of dew that contained the acid on the tips of leaves resulting in turn from the cooling effect of heat radiation, which caused these drops to run off to a leaf edge or tip. Soot was also considered to be a carrier of the acid. The extent of damage appeared to depend on the amount and concentration of the acid in the water droplet or soot particle. The acid apparently diffused out of the droplet in all directions and resulted in a rather uniform appearance in cases where the droplets affected the leaf. The depression in the leaf was small or large, bowl-shaped or jar-shaped, shallow, or tapering in a wedge shape. The injured areas appeared brown on broadleaf species and yellow on conifer species. Acid damage could be found not only on interveinal tissue, but also on the veins.

In 1938, Horicht[225] reported damage to forest trees in the vicinity of soda-ash factories that released hydrogen chloride. He attributed the damage to the acid and noted that conifers were more susceptible than broadleaf species. As will be seen later, the observation on susceptibility is not in accord with observations of others, and no data were presented to support it.

In 1956, Antipov[11] reported hydrogen chloride gas damage to ornamental plants near a chemical factory in the USSR that released fumes once or twice a month. The affected plants included oriental poppy, daisy, belleflower, columbine, bluets, and phlox. Styazhkin[456] reported the death of trees and shrubs in 1957 in the vicinity of the Solikansk magnesium plant (USSR), where unpurified hydrogen chloride gas was emitted through a stack 120 m high at 15 tons/day. The maximal ground-level concentration of 34.0 mg/m^3 was measured 1,000 m from the plant; the maximal ground-level concentration at 3,000 m was 17.3 mg/m^3.

Recently, Hindawi[217] reported damage to trees, shrubs and ornamental plants in an eastern community in the United States in the fall of 1966. Severe damage was evident on specimens of maple, cherry, redbud, rose, and begonia. Hindawi attributed the damage to hydrochloric acid mist and chlorine emitted from a nearby glass manufacturing plant. Although no atmospheric air analyses were made by Hindawi, the damage was probably caused by hydrogen chloride gas or hydrochloric acid emitted by the reduction of silicon tetrachloride in high-temperature ovens to produce the fused silica glass. Hydrogen chloride is a colorless hygroscopic gas and, because of its high solubility in water (82.3 g/100 ml of cold water), readily forms aqueous hydrochloric acid. Under normal atmospheric conditions, it is an aqueous acid aerosol; but in unusually low relative humidity, it is anhydrous hydrogen chloride. The toxic effects of high concentrations of this anhydrous form may be more severe than those of the aqueous form, because of the dehydrating action of the gas on exposed tissues.

In 1968, Wood[520] reported that smoke from the combusion of polyvinylchloride insulation at a wire salvage operation in northern Pennsylvania caused extensive damage to several northern hardwoods and attributed the damage to hydrochloric acid mist; there were no atmospheric air analyses. The damage may well have been caused by the anhydrous or the aqueous phase of hydrogen chloride. Boettner and Weiss[46] reported that hydrogen chloride gas accounts for 58% of the weight loss in the low-temperature fraction of polyvinylchloride combustion.

In 1969, Bohne[48] reported hydrogen chloride gas damage to several shrubs, trees, and flowers near a hospital incinerator.

Symptomatology

The experiments of Haselhoff and Lindau[195] and those of earlier researchers--such as Turner and Christison, Schroeder and Reuss, and Ramann (all cited in Haselhoff and Lindau)--are of limited usefulness, because they were conducted without air circulation over the plants. The gas concentrations used in their experiments were obtained by evaporating hydrochloric acid or by using hydrochloric acid of varying specific gravity in a closed vessel, such as a bell jar. Only a summary of their observations is presented below.

Symptoms observed on broadleaf species by early investigators include discoloration on the margin of leaves and spotting in the central portion of leaves. The discolorations ranged from white to brownish-yellow or red, and sometimes to black. The spots observed in the central portion of the leaves were reported to be transparent, except for small black dots that were thought to be tannin substances. When the gas concentration was increased, the entire leaves collapsed and turned brown. The species tested included roses, buffalo currant, beech, birch, maple, oak, viburnum, apple, pear, and cherry.

On narrow-leaf species, such as grain crops and meadow-grass, the tips of the leaves were affected and turned brown. The edges of the leaves exhibited a similar coloring. High concentrations of the gas caused entire leaves to turn brown and limp.

Conifer species--such as larch, spruce, fir, and pine--exhibited such symptoms as discolored needle tips and yellowing or browning of the needle tips. The affected tips had a sharp border against a green base.

One interesting observation reported in these early experiments was that flower parts were affected. The blue coloring material of flowers was especially sensitive, particularly in chicory and cornflowers. The color change occurred within 12-15 hr. With the exception of two or three reported cases, flower parts are not sensitive to air pollutants. It is interesting to note also that Haselhoff and Lindau[195] concluded from their literature survey and their own experiments that damage to vegetation by the action of fumes containing hydrochloric acid or chlorine on the soil or by the influence of their reaction products in the ground is not probable. Damage to vegetation by such fumes could be brought about only by direct action on the above-ground parts.

Recent observations of field injury by hydrogen chloride gas include those of Hindawi,[217] Wood,[520] and Bohne.[48] Hindawi reported that hydrogen chloride injury on redbud and begonia consisted of a brown-orange color on the margin of the leaf tissue and necrotic spots on the surface of leaves. Premature leaf abscission was also noticed. Damage was reportedly similar to that caused by hydrogen fluoride and sulfur dioxide. Wood[520] reported that hydrogen chloride caused chlorotic flecking of the upper leaf surfaces and red-brown to black necrotic spots on the leaves of northern hardwood species. Tan necrotic flecks and distortion of leaves were observed on the conifer species present in the area. Broadleaves also exhibited leaf cupping.

Means and Lacasse[339] tested the sensitivity of 12 coniferous and broadleaf tree species to hydrogen chloride gas. The fumigations were conducted for 4 hr under controlled conditions at a temperature of 27 C, a relative humidity of 78-85%, and a light intensity of 1.4×10^4 ergs/cm^2-sec. Under these conditions, the only symptom noted on conifer needles was a tip necrosis on white pine at 8 ppm, on balsam and Douglas fir at 12 ppm, and on Norway spruce at 19 ppm. Austrian pine and arborvitae were not injured at concentrations of 18 and 43 ppm, respectively. Symptoms on broadleaf species included marginal and interveinal necrosis and necrotic flecking. Tuliptree was injured at 3 ppm, European black alder and black cherry at 6 ppm, and sugar maple and Norway maple at 7 ppm. Red oak was not injured at concentrations up to 13 ppm.

Shriner[426] undertook extensive experiments to determine symptom response of tomato (cultivar Bonny Best) and chrysanthemum (cultivar Neptune) to hydrogen chloride under controlled conditions. In tomato, severe injury in the form of bronzing occurred at a concentration of 4 ppm for 2 hr at a relative humidity of 70% and a temperature of 30 C, but a concentration of 10 ppm was required to produce a similar effect for the same exposure duration when the humidity was 50% and the temperature was 31 C. Marginal leaf necrosis and injury to the petiole occurred at a concentration of 5 ppm for 2 hr at a relative humidity of 81% and a temperature of 33 C, but again a concentration of 10 ppm was needed to produce similar symptoms when the relative humidity was lowered to 55% at a temperature of 31 C for 2 hr. Symptoms of glazing on the underside of the leaf, leaf tipburn, and necrotic flecking were produced at a concentration of 3 ppm for 2 hr when the relative humidity was 65-72% and the temperature 31-33 C; a concentration of 8 ppm for 3 hr was needed to cause those symptoms at a relative humidity of 35%. No visible injury developed when the concentration was 2-5 ppm for periods of 2-3 hr when the relative humidity was 55-60% and the temperature 30-31 C. Even a concentration of 8.5 ppm for 3 hr caused no injury when the relative humidity was 23% at a temperature of 31 C.

Chrysanthemum was much more resistant to hydrogen chloride than tomato. The plants were severely injured, with bronzing as the predominant symptom, when they were exposed to 8-23 ppm for periods of 4 and 2 hr, respectively, and relative humidity of 65-70% and temperature of 30-31 C. Marginal necrosis and petiole injury occurred at 3.5-8.5 ppm, respectively, for 3-hr fumigations at 31 C and relative humidities of 65 and 45%, respectively. Glazing on the underside of the leaf, tipburn, and necrotic flecking occurred when the concentration was 6 ppm for 5 hr at 60% relative humidity or 12 ppm for 2 hr at 52% relative humidity. No injury developed at a concentration of 2.7 ppm for 2 or 3 hr at a relative humidity of 60% and 30 C.

Chronic fumigations of tomato (Bonny Best) were performed by Godish[175] and Godish and Lacasse[177] in 1970. Chlorosis was the dominant symptom observed when plants were fumigated at 0.70 ppm for 10 hr/day for 2 days. The chlorosis was generally interveinal and occurred most often on younger leaves and leaves of intermediate maturity. A severe upward curling of the leaf margins was observed occasionally after the first 10 hr of fumigation and was almost always present after the second 10 hr. At 0.40 ppm for 8 hr/day for 6 days, no visible symptoms were observed on greenhouse-grown plants during winter. However, for greenhouse-grown plants during May and June, chlorosis developed at that concentration after the third or fourth consecutive fumigation.

Haselhoff and Lindau[195] summarized the work of Wieler and Hartleb dealing with the physiologic impact of hydrochloric acid. However, their experiments were performed by immersing plants in water with hydrochloric acid and carbon dioxide and counting the number of bubbles evolved to determine assimilation rates. In the hydrochloric acid solution, the number of bubbles always decreased and the gas bubbles were always smaller, indicating a considerable decrease in assimilation. The plants tested included waterweed, beans, oaks, and red beeches. They concluded that sulfurous acid decreases transpiration and hydrochloric acid decreases assimilation.

Godish[175] and Godish and Lacasse[176] also reported several metabolic effects associated with acute and chronic hydrogen chloride fumigations. With acute fumigations of 8-10 ppm for 2 hr at a relative humidity of 40-50% (when few or no symptoms developed), a 20-30% stimulation of the respiration rate was detected. The respiration rate returned to normal within 24 hr. As the degree of injury increased, respiration rate became more and more variable, and no statistically significant changes could be detected.

Photosynthesis rates after fumigation at 8-10 ppm and a relative humidity at or below 40% were about 90% of those of control plants. These rates were corrected for respiration. Although the rates were not statistically significant, the changes indicate a trend toward inhibition of photosynthesis. No visible injury was present under these circumstances. In situations in which symptoms developed (10-50% of the leaf area injured), photosynthesis was reduced by as much as 25% on a unit chlorophyll basis (i.e., on the basis of the amount of chlorophyll present, rather than on the basis of the leaf area, because of the obvious leaf injury).

Transpiration rates were also decreased by acute fumigation. At its lowest point, the average transpiration rate of fumigated plants was 59% of rate of control plants. Transpiration returned to normal during the 12-hr dark period after fumigation.

When plants were fumigated at 0.70 ppm for 10 hr/day for 2 days, there was no significant difference in respiration rate between control and fumigated plants when measured at 0, 24, and 48 hr after fumigation and when the rate was based on fresh weight. However, a significant stimulation of respiration of fumigated plants was evident in each of the sampling periods on a dry-weight basis.

At 0.40 ppm for 8 hr/day for 6 days, respiration rate at 0 and 24 hr after fumigation was significantly reduced on either a fresh-weight or a dry-weight basis.

The photosynthesis rate measured before chlorosis became visible was significantly decreased on a unit area basis. However, no differences were observed when the rate was expressed on a chlorophyll basis. After symptom development (24 hr after fumigation), there was no difference in the photosynthesis rate based on leaf area. However, fumigated plants had a significantly higher rate if the rate was based on total chlorophyll. It appears that, at or near saturating light intensities, the rate of photosynthesis in fumigated plants is higher if photosynthetic efficiency is measured under various light intensities based on unit chlorophyll content. At the highest light intensity (7.6×10^4 ergs/cm^2-sec), there were significant differences in the rate of photosynthesis between the two groups. Thus, it appears that, if only a small amount of chlorophyll is destroyed, the remaining chlorophyll is better able to utilize light energy. However, if the same data are based on unit leaf area, the control plants have a significantly higher rate of real photosynthesis at light intensities below saturation. There is no difference between the two groups at the highest light intensity. These differences clearly indicate that it would not be advantageous to attempt measurement of leaf function impairment by using chlorophyll content as an index of injury.

Transpiration rates of plants at chronic fumigation concentrations were reported to be slightly decreased during exposure at 0.70 ppm. Water loss was significantly reduced (83% of the control value) during the 4 hr after fumigation, but quickly returned to normal by the end of the 4-hr period.

Godish[175] also measured chlorophyll and pheophytin concentrations after fumigation at 0.70 ppm for 10 hr/day for 2 days. Significant changes in total chlorophyll and total pheophytin were detected immediately after fumigation and 16 hr later. Chlorophyll destruction or conversion did not result in pheophytin formation. Ratios of chlorophyll a to chlorophyll b and pheophytin a to pheophytin b did not indicate preferential destruction of individual pigments. Because no increase in pheophytin concentration was found in plants exposed to hydrogen chloride gas, Godish concluded that the observed destruction or conversion of chlorophyll was clearly not due to pheophytinization. The action of hydrogen chloride gas on chlorophyll is probably not due solely to the acidic properties of the gas.

Fisher[145] fumigated bean plants (pinto III) simultaneously with ozone and hydrogen chloride gas. The injury observed depended on the concentrations of the gases. With ozone at 0.10-0.20 ppm and hydrogen chloride gas at 1.5-3 ppm for 2 hr, the injury consisted of an upper-leaf-surface stippling and flecking, marginal necrosis, veinal and interveinal tissue collapse on the underside of the leaf, or interveinal tissue collapse of the underside of the leaf alone. With ozone at 0.20-0.25 ppm and hydrogen chloride at 3-4 ppm, the injury consisted of flecking or stippling with collapse of both surfaces of the leaf. Symptom expression was highly variable, and only one symptom type was present on a given leaf. The following mathematical relationship was derived for ozone-hydrogen chloride fumigations:

$$R = -6.23 - 0.10\,[O_3] + 0.02\,[O_3]^2 + 0.89\,[HCl] + 0.52\,[HCl]^2 .$$

The equation has the following limits:

$0.0 < [O_3] < 25.0$, where $[O_3]$ is the ozone concentration in parts per hundred million.

$0.0 < [HCl] < 4.0$, where $[HCl]$ is the hydrogen chloride gas concentration in parts per hundred million

R is considered to be equal to zero, if it is equal to or less than zero, where R is the pinto bean response expressed as percent leaf injury.

The equation describes approximately 90% of the data generated in Fisher's experiments.

Fisher[145] reported that the threshold concentrations for injury to pinto beans in a 2-hr fumigation were approximately 2.6 ppm for hydrogen chloride gas alone and 0.18 ppm for ozone alone. When plants were fumigated with both pollutants simultaneously, the injury threshold concentration for hydrogen chloride gas was lowered to 1.2 ppm, but remained at 0.18 ppm for ozone.

Morphology and Histopathology of Hydrogen Chloride Injury

Haselhoff and Lindau[195] reported that the cells in white limp leaves of fumigated rye appeared heavily bleached and shriveled, and in some cells in the vicinity of the vascular bundles there were brown or black deposits consisting of tannin. In pea leaves, the grains of chlorophyll appeared swollen, and tannin deposits filled some cells nearly completely and colored them black. Roses exhibited even heavier tannin deposits. Montana pine exhibited a pale discoloration of the needle, with browning and drying spreading from the tip. In the assimilation cells, the grains of chlorophyll were bleached out and were often no longer clearly recognizable in outline. The contents of the cell were often bunched together, later turned brown with continued drying, and finally disappeared, except for small remnants. In the first stages, often only the cuticula appeared brown, but the coloring of the membrane later extended inward, and finally the greatest part of the membranes became brown at the dry areas. Haselhoff and Lindau also reported an observation by Wieler related to the red coloring of the guard cells of spruce.

Shriner[426] and Shriner and Lacasse[428] examined the effect of hydrogen chloride gas in histologic studies and related the type of visible symptoms observed to the specific leaf tissues that were affected. They reported that the under-leaf-surface glazing symptom appeared to be a result of the collapse of the lower epidermal cells. This was particularly evident in tomato. They attributed this to the relatively large amount of air space adjacent to the lower epidermis inside the leaf, in contrast with the palisade tissue. The bronzing symptom on both tomato and chrysanthemum appeared to result from the collapse of the lower epidermis, the spongy mesophyll, and occasionally the palisade mesophyll and upper epidermis. Microscopic symptoms observed by Shriner resemble those described by Solberg and Adams[443] for hydrogen fluoride and sulfur dioxide and by Bobrov[44] for smog. Shriner concluded from his histologic studies that the gas entered the plants through the stomata because tissues nearest the stomata were always the first to be damaged. The substomatal injury observed closely resembles what Bobrov[45] described as "dehydration" of cells lining the substomatal cavities of annual bluegrass damaged by smog. The bronzing symptom observed by Shriner in tomato and chrysanthemum was very similar to the "tan-colored spot" symptom caused by hydrogen fluoride on apricot and caused by sulfur dioxide on pinto bean.

According to Shriner, the order of tissue damage for tomato after entry through the stomata appears to be as follows: collapse of adjacent lower epidermal cells and then disorganization and collapse of the spongy mesophyll. Depending on the severity of damage, the palisade mesophyll may or may not collapse, and then the upper epidermis. In chrysanthemum, collapse of the tissues was not as severe as in tomato. Shriner postulated that this was because chrysanthemum cell walls were thicker than those of tomato.

Factors That Modify Plant Response

Shriner[426] listed a number of factors affecting the response of tomato and chrysanthemum to hydrogen chloride gas. Of prime importance is the dose (concentration and length of fumigation). The relative frequency and abundance of stomata also appear to be important in the sensitivity of plants to this gas.

The relative humidity of the exposure environment appears to be the dominant factor in symptom expression. The results obtained by Shriner[426] and Godish[175] indicate that there is a relative humidity threshold above which injury will be severe and below which injury will be minimal for a given dose of the gas. Although much time and effort have been expended in numerous fumigations to determine precisely what that threshold relative humidity is, the question remains unresolved. The problem lies in the fact that the gas is hygroscopic. There are indications that, at relative humidities above 80%, the damage is typical of that caused by acid--i.e., small, discrete flecks on the exposed leaves. At relative humidity below 80%, the damage is typical of that caused by gas.

Cell wall thickness and amount of intercellular space appear to influence the severity of symptom expression. It should be noted, however, that the data base for this conclusion is extremely limited.

Age of tissue appears to be important in symptom expression in relation to the amount of chloride taken up by or translocated within plants. Shriner's data suggest either that semimature tissue in tomato is capable of greater uptake of chloride or that chloride can be more readily translocated to growing points in that species. It is interesting to note that, when the source of chloride is the soil, a number of plant species normally tend to accumulate chloride in the petiole. Shriner reported petiole damage in both tomato and chrysanthemum, suggesting some translocation from lower leaves. It is also interesting that the semimature tissue of tomato, which showed the greatest increase in chloride content, did not necessarily show the severest symptoms. A possible explanation is that, as the leaf continues to grow and expand, the chloride present in the leaf is diluted.

Shriner's chrysanthemum data show that chloride accumulates in mature tissue in that species, although large increases were also noted in semimature tissue. Because Shriner fumigated chrysanthemum at much higher concentrations of hydrogen chloride (7-18 ppm) than tomato (2-5 ppm), it is not possible to state conclusively that translocation or greater uptake occurs in tomato, but not in chrysanthemum.

Sensitivity

Although Haselhoff and Lindau[195] reported large differences in species sensitivity to hydrogen chloride gas, the value of their data should be questioned, because they were obtained without adequate air circulation over the plants. The results obtained by Means and Lacasse[339] represent the only recent determination of sensitivity of plant species to hydrogen chloride gas under controlled conditions. Unfortunately, only a few forest tree species were tested, and the experiments were designed to determine the dose at which acute injury would occur. Their data do suggest, however, that broadleaf plants are generally more sensitive than coniferous plants. Limited experiments by Thomas[476] on sugar beets suggested that the marking threshold concentration for a few hours of exposure was about 10 ppm.

The results of work by Antipov[11] and Means and Lacasse[339] with respect to sensitivity of plants to hydrogen chloride are summarized in Table 6-2.

Accumulation

Shriner[426] and Shriner and Lacasse[427] measured chloride concentrations in tomato plants at various intervals after fumigation. Significant increases in chloride content occurred in all parts of fumigated plants. Chloride concentration in foliar portions was higher immediately after and 24 hr after fumigation and then decreased gradually. Actively growing tissue appeared to have a greater tolerance for chloride than older leaves, which exhibited symptoms readily with smaller amounts of chloride taken up. A 0.14% increase in chloride occurred in immature secondary leaves after fumigation at 3.5 ppm for 2 hr; an increase of 0.10% occurred in mature secondary leaves. Roots showed the smallest increase, 0.002%.

Shriner measured chloride content based on fresh weight of tissues. Tissues were homogenized in a top-drive macerator in water. The macerate was centrifuged at 3,500 rpm for 15 min, and the supernatant was filtered. The clear extract was buffered with 0.1 N nitric acid-10% acetic acid and titrated with a Buchler-Cotlove automatic chloride titrator. Repeated extracts of the pellet were titrated. The results showed that the initial extraction contained 95 ± 2% of the free chloride in the cell sap of the test plant tissues.

TABLE 6-2

Relative Sensitivity of Plants to Hydrogen Chloride[a]

Sensitive	Intermediate	Resistant
Caespitose phlox	Black cherry	Adonis
Columbine	Chrysanthemum	Arborvitae
Cornflower	European black alder	Austrian pine
Garden daisy	Norway maple	Balsam fir
Oriental poppy	Pinto bean	Douglas fir
Tomato	Sugar maple	Garden iris
Tuliptree	White pine	Garden lupine
		Garden peony
		Goldenrod
		Larkspur
		Lily-of-the-valley
		Norway spruce
		Paniculate phlox
		Pheasant's eye pink
		Plantain lily
		Red oak
		Sweet William

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[a] Data from Antipov[11] and Means and Lacasse.[339]

It should be noted that determination of elements in plant material based on fresh weight can lead to errors. This is particularly true in dealing with severely injured plants. The injured tissues become disrupted and lose moisture. This decrease in fresh weight would be accentuated over time. It would be preferable to base measurements on dry weight.

Mimicking Symptoms

The glazing symptom was first reported for peroxyacetylnitrate (PAN) injury in California on a number of plant species.[468] This symptom has been observed elsewhere in the United States and has been generally attributed to PAN. PAN has not been measured in areas other than California or Utah, because of lack of instrumentation. It is possible that PAN has not been solely responsible for this symptom every time it has been observed.

Marginal leaf scorch has been reported to be caused by salt (sodium or calcium chloride) used on highways for deicing.[189] This symptom closely resembles the marginal burning caused by hydrogen chloride gas.

Appendix to Chapter 6

Common and Scientific Names of Plants

Common Name	Scientific Name
Adonis	*Adonis* sp.
Alfalfa	*Medicago sativa* L.
Annual bluegrass	*Poa annua* L.
Apple	*Pyrus* sp. L.
Apricot	*Prunus armeniaca*
Arborvitae	*Thuja occidentalis* L.
Ash	*Fraxinus* sp. L.
Austrian pine	*Pinus nigra* Arnold
Azalea	*Rhododendron* sp. L.
Balsam fir	*Abies balsamea* (L.) Mill.
Basswood	*Tilia* sp. L.
Bean	*Phaseolus*
Beech	*Fagus* sp.
Begonia	*Polygonum* sp.
Bellflower	*Campanula* sp. L.
Birch	*Betula* sp.
Blackberry	*Rubus* sp.
Black cherry	*Prunus serotina* Ehrh.
Bluets	*Houstonia* sp. L.
Box elder	*Acer negundo* L.
Bramble	*Rhodotypos* sp. Siev. and Zucc.

Common Name	Scientific Name
Buckwheat	Fagopyrum sagittatum Gilib.
Buffalo currant	Ribes aureum Wendland f.
Cactus	Cactaceae sp.
Caespitose phlox	Phlox sp. L.
Cheeseweed	Malva parviflora L.
Cherry	Prunus sp. L.
Chickweed	Stellaria sp. L.
Chicory	Cichorium intybus
Chinese holly	Ilex sp. L.
Chrysanthemum	Chrysanthemum sp. L.
Coleus	Coleus sp.
Columbine	Aquilega sp. L.
Corn	Zea Mays L.
Cornflower	Centaurea cyanus L.
Cosmos	Cosmos sp. Cav.
Cowpea	Vigna sinensis (L.) Endl.
Crab apple	Pyrus sp. L.
Cucumber	Cucurbita sp. L.
Dahlia	Dahlia sp.
Daisy	Chrysanthemum sp. L.
Dandelion	Taraxacum officinale Weber
Dogwood	Cornus sp. L.
Douglas fir	Pseudotsuga taxifolia (Poir) Britt.
Dragon tree	Dracaena draco

Common Name	Scientific Name
Eggplant	*Solanum* melongena L.
Elm	*Ulmus* sp. L.
European black alder	*Alnus* *glutinosa* (L.) Gaertn.
Fir	*Abies*
Garden daisy	*Chrysanthemum* sp. L.
Garden iris	*Iris* sp. L.
Garden lupine	*Lupinus* sp. L.
Garden peony	*Paeonia* sp.
Geranium	*Geranium* sp. L.
Ginkgo	*Ginkgo* *biloba* L.
Globe-amaranth	*Gomphrena* *globosa* L.
Goldenrod	*Solidago* sp. L.
Hemlock	*Tsuga* sp. (Endl.) Carr.
Horse-chestnut	*Aescubus* *hippocastanum* L.
Hybrid tea	*Theaceae*
Italian prune	*Prunus* *domestica* L.
Kentucky bluegrass	*Poa* *pratensis* L.
Lamb's quarter	*Chenopodium* sp. L.
Larch	*Larix* sp. Mill.
Larkspur	*Delphinium* sp. L.
Lettuce	*Lactuca* sp. L.
Lilac	*Syringa* sp. L.
Lily-of-the-valley	*Convallaria* sp. L.
Linden	*Tilia* sp. L.

Common Name	Scientific Name
Loblolly pine	Pinus taeda L.
Maple	Acer sp.
Meadow-grass	Poa sp. L.
Mignonette	Reseda lutea L.
Mustard	Brassica sp. L.
Myrtle	Vinca minor L.
Nasturtium	Nasturtium sp. R. Br.
Nettle-leaf goosefoot	Chenopodium sp. L.
Norway maple	Acer platanoides L.
Norway spruce	Picea abies L. Karst.
Oak	Quercus sp. L.
Onion	Allium cepa L.
Oregon grape	Mahonia (Berberis) aquifolium
Oriental poppy	Papaver sp. L.
Osier	Salix viminalis L.
Oxalis	Oxalis sp. L.
Paniculate phlox	Phlox paniculata L.
Pea	Pisum satium
Peach	Prunus persica (L.) Batsch.
Pear	Pyrus sp. L.
Pepper	Capsicum sp.
Petunia	Petunia sp. Juss.
Pheasant's eye pink	Dianthus sp. L.
Phlox	Phlox sp. L.

Common Name	Scientific Name
Pigweed	*Chenopodium* sp. L.
Pine	*Pinus* sp.
Pin oak	*Quercus palustris* Muenchh.
Pinto bean	*Phaseolus vulgaris* L.
Plantain lily	*Hosta plantaginea* (Lam.) Archers
Plum	*Prunus* sp. L.
Radish	*Raphanus sativus* L.
Red beech	*Fagus* sp. L.
Redbud	*Cercis* sp. L.
Red clover	*Trifolium pratense* L.
Red currant	*Ribes sativum* Syme
Red oak	*Quercus rubra* Du Roi
Rose	*Rosa* sp. L.
Rye	*Elymus* sp. L.
Scotia bean	*Phaseolus* sp. L.
Shortleaf pine	*Pincus echinata* Mill.
Silverbell-tree	*Halesia* sp. Ellis
Slash pine	*Pinus caribaea* Morelet
Smartweed	*Persicaria* sp. L.
Spruce	*Picea* sp.
Squash	*Cucurbita* sp. L.
Strawberry	*Fragaria* sp. L.
Sugar beet	*Beta vulgaris* L.
Sugar maple	*Acer saccharum* Marsh.

Common Name	Scientific Name
Sunflower	Helianthus sp. L.
Sweetgum	Liquidambar styraciflua L.
Sweet william	Dianthus barbatus L.
Tobacco	Nicotiana tabacum L.
Tomato	Lycopersicum esculentum Mill.
Tree of heaven	Ailanthus altissima (Mill.) Swingle
Tulip tree	Liriodendron tulipifera L.
Viburnum	Viburnum sp.
Virginia creeper	Parthenocissus sp. Planch.
Wandering Jew	Tradescantia sp. L.
Waterweed	Elodea sp. Michx.
White beech	Fagus sp. L.
White pine	Pinus strobus L.
White thorn	Crataegus sp. L.
Zinnia	Heliopsis sp. Pers.

CHAPTER 7

PROPERTY DAMAGE AND PUBLIC NUISANCE

This chapter deals primarily with chlorine and hydrogen chloride as nuisances. That is, such subjects as acute and chronic toxicity to humans, animals, and plants will be avoided. Attention will be focused on the effects of chlorine and hydrogen chloride on aesthetics and as chemical irritants. Also to be considered are their influence as agents that initiate or aggravate corrosion of and damage to building materials and other property.

HISTORICAL SURVEY OF AIR POLLUTION BY HYDROGEN CHLORIDE

The possibility of airborne emission of chlorine and hydrogen chloride is unavoidably associated with their manufacture and use. One of the first large sources of hydrogen chloride was the use of the Leblanc process for the manufacture of soda ash.[311] This process can be summarized by the following reactions:

$$H_2SO_2 + 2NaCl \longrightarrow 2HCl \uparrow + Na_2SO_4,$$

$$Na_2SO_4 + 2C \longrightarrow 2CO_2 \uparrow + Na_2S,$$

$$Na_2S + CaCO_3 \longrightarrow Na_2CO_3 + CaS,$$

$$CaS + CO_2 + H_2O \longrightarrow CaCO_3 + H_2S, \text{ and}$$

$$H_2S + 2O_2 \longrightarrow H_2SO_4.$$

The net overall reaction is the production of soda ash and hydrogen chloride (the intermediate products are recycled):

$$2NaCl + H_2O + CO_2 \longrightarrow 2HCl \uparrow + Na_2CO_3.$$

Naturally, the hydrogen chloride produced as a byproduct of soda ash could have been recovered as hydrochloric acid by condensation or scrubbing. When the Leblanc process was introduced into Great Britain in 1818, it was carried out on a small scale and the practice was to roast sulfuric acid with salt in an open furnace. As a consequence of this, hydrogen chloride was released to the atmosphere. The demand for hydrochloric acid and products that might have been manufactured from it was insufficient to permit marketing of all the acid produced; so most recovered hydrochloric acid would have gone to the sewer, and one pollution problem would have been exchanged for another.

With the passing years, the production of Leblanc soda ash grew from 90,000 kg (100 tons) in 1818 to more than 81 x 10^6 kg (90,000 tons) in 1864. The technology for condensing and scrubbing hydrogen chloride-bearing streams was well advanced by that time, but often the financial incentive to ensure the complete recovery of the hydrochloric acid did not exist, because of lack of demand for the product. By 1864, it was customary to condense and scrub the effluent gases in packed columns and to vent the remaining gas through stacks as high as 150 m. However, because of the increased production, the total amount of hydrogen chloride vented to the atmosphere had increased beyond that of earlier times, when no attempts were made to recover the acid.

According to Lunge,[311] (p. 306) "the destruction of the vegetation round the alkali-works was only too evident....It was impossible to ignore the nuisance caused by the smell, and the worse one that iron objects of all kinds, locks, window-fittings, gutters, etc., could not be kept from rusting, that tools of mechanics were at once blunted, and that even window-curtains were destroyed in a very short time." Clearly, some type of controlling legislation was needed.

On July 13, 1863, the House of Commons passed an "Act for the More Effectual Condensation of Muriatic Acid Gas in Alkali Works."[10] This law, which is often referred to as the Lord Derby alkali act, after one of its chief sponsors, was to come into force on January 1, 1864, and expire on July 1, 1868. The alkali act was a considerable departure from previous legislation. Before 1863, some jurisdictions had passed laws banning chemical plants, including Leblanc process plants, from within their limits. This solved the local problem, but usually resulted only in a plant's relocation to another site. Of course, this in no way reduced pollution within Great Britain. Instead of this approach, the alkali act recognized the desirability of the manufacture of soda ash and set up a system of monitoring and control to reduce the emission of hydrogen chloride that inevitably accompanies production of soda ash by the Leblanc process.

The alkali act had four important provisions:

1. Emission of hydrogen chloride from Leblanc process plants were to be no greater than 5% of the total hydrogen chloride produced.

2. An inspection system was set up, and the inspectors were empowered to monitor plant emission whenever they desired. If in their opinion the plant emission exceeded the limit over a 4-hr period, the operator could be brought into court.

3. Operators of Leblanc process plants were required to register their plants with the inspectors.

4. Operators convicted of a first offense were subject to a fine not exceeding 50 pounds. Each additional conviction carried a fine not to exceed 100 pounds, and this fine could be applied for each successive 24-hr period in which a violation was proved.

Thus, the alkali act established a limit on emission, provided a system of compulsory inspection, required registration of emission sources, and penalized convicted violators. This piece of legislation, unique at the time, set a precedent for pollution control legislation throughout the world. However, a law is useful only if it is complied with and enforced.

The year after the act went into force, all 64 Leblanc process plants reported on were in compliance with the 5% emission standard, and 33 were emitting none or no more than 0.1% of the total hydrogen chloride produced.[524] In 1866, all plants averaged less than 1% emission.[473] In 1867, the first prosecution under the alkali act took place. The Bridgewater Smelting Company was convicted and fined 50 pounds for the release of large quantities of hydrogen chloride.[144]

The alkali act was a marked success, and there was said to be substantial improvement in the environment of the neighborhoods of chemical works. Therefore, the act, which was to have expired in 1868, was renewed and made perpetual.[147]

However, the alkali act needed improvement. It said nothing about other sources of hydrogen chloride, such as potential consumers, nor did it include other offensive gases. Thus, it was amended in 1874[147] to require that the emission of noxious gases be controlled by the best practicable means. Noxious gases were defined as chlorine, oxides of nitrogen, hydrogen sulfide, and oxides of sulfur, except those arising from the combustion of coal. The emission standard for hydrogen chloride was further defined as not to exceed 0.2 grain/ft^3 (about 0.46 g/m^3).

In the 110 years since the passage of the alkali act, it has been amended periodically to include every conceivable gas or fume that might be considered harmful, and it now governs all sectors of industry. Through these many alterations and extensions, the rational principles incorporated in the alkali act of 1863 have remained unchanged.

Such laws did not evolve in the United States, because the gross, continuous emission of hydrogen chloride of the early days of the Leblanc process in Great Britain did not occur in the United States. In fact, the Leblanc process was never used in the United States. Thus, in the early days of the chemical industry in the United States, hydrogen chloride was not produced as a largely or partially useless byproduct.

GENERALIZED CORROSION

Chlorine, hydrogen chloride, and the acid solutions derived from them when they are dissolved in water are considered very corrosive. Accordingly, many studies have been carried out to determine their corrosive properties and to evaluate the rate at which they attack materials. These studies have been limited mostly to the commercially significant concentrations in the gaseous, liquid, and aqueous phases. With the exception of a very rare occurrence of catastrophic failure of equipment that results in a massive release of chlorine or hydrogen chloride, those concentrations are much greater than the ones with which we are primarily concerned. There are some data that pertain specifically to the very dilute gases and solutions that are considered here, and other information can be inferred from fundamentally similar systems of acids, oxidizing gases, and electrolytes. Before a discussion of corrosion related specifically to chlorine and hydrogen chloride, is it important that something of an understanding of atmospheric corrosion be developed.

Atmospheric corrosion of materials is a highly complex subject and can hardly be treated fully here. But it is necessary to consider what contributes to it. It must be realized that all the metals most commonly used should be expected to react to form compounds, usually oxides, in the earth's atmosphere. If they do not or if they do so only very slowly, it is because corrosion or reaction is retarded by a protective coating. The protective coating may have been applied purposely, such as paint, or it may have formed spontaneously, such as the iron oxide film on steel. Any agent that either attacks the coating or interferes with its formation will accelerate corrosion beyond the "normal" rate.

The normal rate of atmospheric corrosion is influenced by temperature, relative humidity, sunlight, and the presence and characteristics of particulate matter and trace gases. Most chemical reactions are accelerated by an increase in temperature, but a temperature increase may also slow corrosion by decreasing the relative humidity. In the absence of moisture, little if any corrosion takes place, even in a very polluted atmosphere; none takes place in an unpolluted atmosphere. A film of water will adsorb on a surface to a degree that depends on the relative humidity and the affinity of the surface for water molecules. When the surface is completely clean and dry, the circuit is open; no current can flow, and no electrochemical reaction takes place. When water is adsorbed on the surface, it acts as an electrolyte, allowing current to flow, and corrosion takes place. Substances, such as carbon dioxide, that dissolve in the adsorbed water layer and cause additional ions to be formed by hydrolysis aggravate the situation by increasing the number of ions available to carry current.

Inert particulate matter can cause erosion by impingement, but we are concerned here with its ability to act as an adsorption site for chemicals and moisture, which accelerate corrosion. Also, particulate matter can be acid mists or solid particles, such as sodium chloride, which supply electrolyte to the water film and often make corrosion products more soluble, helping to expose fresh surface to attack.

Many trace gases, including chlorine and hydrogen chloride, accelerate corrosion through some of the mechanisms cited. They dissolve in the adsorbed water film to supply electrolyte and can in fact cause adsorption of additional water by lowering the vapor pressure of the film. Some can also effectively increase the solubility of corrosion products through changes in the acidity of the water film, and the ions produced in the water film can increase the solubility of corrosion products, tending to expose fresh surfaces to attack.

Anhydrous chlorine and hydrogen chloride are stored in mild steel tanks and conveyed in pipelines and containers fabricated from mild steel. At ordinary temperatures, corrosion is negligible. But chlorine and hydrogen chloride are among the most corrosive of chemicals. The reason that corrosion of the steel does not occur is the absence of moisture. Corrosion proceeds via the adsorbed water film, and this mechanism will prevail as long as the temperature of the material is above the dewpoint of the water vapor in the surrounding atmosphere; below this temperature, bulk water will condense. However, in the latter case, the chemistry of the process will be essentially the same. The corrosive properties of chlorine and hydrogen chloride are, therefore, inevitably related to the properties of the solutions that are formed when they dissolve in water.

Chlorine dissolves in water and, hydrolyzing to some degree, forms hypochlorous and hydrochloric acid. These ionize to form hydrogen ions and, respectively, hypochlorite and chloride ions:

$$\begin{tikzcd} HOH + Cl_2 \arrow[r, shift left] & HOCl \arrow[l, shift left] \arrow[d, shift left] & + & HCl \arrow[d, shift left] \\ & H^+ + OCl^- \arrow[u, shift left] & & H^+ + Cl^-. \arrow[u, shift left] \end{tikzcd}$$

Hypochlorous acid is a weak acid and can be considered essentially not ionized. It is also a strong oxidizing agent and decomposes to form atomic oxygen and hydrochloric acid:

$$HOCl \longrightarrow O + HCl.$$

Hydrochloric acid is a strong acid and, for practical purposes, can be considered completely dissociated. The term "strong" should not be construed to mean highly concentrated, inasmuch as the concentrations dealt with here are very low.

The corrosiveness of chlorine dissolved in water is due to four factors:

1. It is a strong oxidizing agent and can oxidize metals, their protective coatings, and other materials.

2. It supplies a strong acid that can dissolve the passive, protective oxide film on metals, exposing a fresh metallic surface to additional atmospheric corrosion and can also dissolve the calcium carbonate contained in building materials, such as limestone.

3. It supplies electrolyte, which accelerates galvanic or electrochemical corrosion by increasing the conductivity of the adsorbed water layer.

4. It supplies chloride ion, which enhances corrosion of some metals by the formation of chloride complexes that aid in the solubilization and dispersion of corrosion products that, in its absence, might remain to form a passive barrier. Chlorine ions are particularly offensive, because they can cause intergranular corrosion and pitting, which may far outweight apparent overall corrosion.

Hydrogen chloride dissolves in water to form hydrochloric acid, which is, of course, no different from that formed when chlorine dissolves in water.

Its corrosiveness is due to the last three properties responsible for the corrosiveness of chlorine.

It has been conceded that examples of economic damage caused by the corrosive attack of trace amounts of atmospheric chlorine on metals and other materials are lacking in the literature. Stahl[446] (p. 23) states that "the high reactiveness of chlorine with almost all metals (including iron, zinc, tin, silver, and copper) as well as non-metals (including most organic compounds) suggests that chlorine in sufficiently high concentrations would corrode metals, discolor and damage painted materials, and damage textile fibers." The preceding statement is inarguable. However, it is not known what concentrations are sufficiently high to accelerate corrosion rates significantly beyond what is considered normal. The key word here is "significantly." One might reason that any amount of chlorine would be sufficient to cause an increase in the rate of atmospheric corrosion. For practical purposes, what is of interest is the threshold concentration at which an observable increase in the rate of atmospheric corrosion causes economic loss or damages the aesthetic properties of the surroundings.

A great deal of material regarding the corrosive properties of chlorine has been generated.[461,530] This information, however, is of negligible value, because it deals with concentrations that would never be reached in the atmosphere. Only a few references have been uncovered concerning accelerated atmospheric corrosion due to the presence of chlorine.[76] A silver chloride tarnish, in addition to silver sulfide, appeared on a silver test specimen at one of the test sites where a peak chlorine concentration of 7 ppb and a median chlorine concentration of 1.2 ppb were observed. It is important to note that other pollutants--such as hydrogen sulfide, nitrogen oxides, hydrogen fluoride, ammonia, ozone, and particulate matter--were also present, most often in much larger concentrations. Therefore, one cannot say what the influence of chlorine by itself was. However, the test does supply some useful information, in that chlorine will probably always be accompanied by some of the other chemicals in any industrialized area where chlorine is present.

Test panels have been placed on the roofs of buildings in a chlor-alkali plant to determine the corrosion rate of aluminum and steel in the atmosphere.[172] In areas of the plant most likely to be exposed to chlorine in the atmosphere, the corrosion rate of mild steel was 0.3-1.0 mil/yr (7.6-25.4 μm/yr), except at an open brine storage tank, where the corrosion rate was 5.3 mils/yr (134.6 μm/yr). This last value is rejected, because the brine is the obvious cause of accelerated corrosion. For comparison, at three other areas that were least likely to be exposed to chlorine or other chemicals from the plant, the corrosion rates were <0.1, 0.1, and 0.4 mil/yr (<2.5, 2.5, and 10.2 μm/yr). Unfortunately, no data were given on the atmospheric concentration of chlorine. Also, it must be recognized that many other chemical species would be expected to be present in the atmosphere of the highly industrialized area. The corrosion rates cited would not result in any economic losses, because corrosion rates of 1 mil/yr (25.4 μm/yr) or less are considered insignificant with respect to structural integrity. However, staining with iron oxide might be considered aesthetically displeasing.

In another study, the atmosphere at various locations within a chlorine plant was simulated by mixing chlorine or hydrogen chloride and chlorine with moist air.[157] The results are presented in Table 7-1. The concentration of chlorine is not given, nor is the water content of the air which can be significant in determining the corrosion rate. The authors state that the variation in the corrosion rate of steel is probably due to differences in the chlorine content of the atmosphere to which the test specimens were exposed.

TABLE 7-1

Corrosion Rates of Various Metals Exposed to Chlorine and Hydrogen Chloride in a Chlorine Plant[a]

Exp. No.	Corrosion Rates, Mils Per Year										
	Ti	Zr	Ni	Monel	Hast. C	Chlorimet 3	304	316	Al 6061	Copper	Mild Steel
1	0.002	0.03	....	0.01	....	......	....	0.0002	0.05^{1}	0.09	3
2	0.005	$6^{2,5}$	6^{1}	13	....	......	7^{7}	13^{7}	33^{7}	20^{6}	38
3	0.01	6^{3}	8	28	....	......	$10^{3,6}$	$8^{3,6}$	96	55^{6}	90
4	0.004	4^{2}	5^{1}	6^{1}	....	......	$3^{2,6}$	$4^{3,6}$	18	21^{6}	58
5	0.004	0.02	0.05	0.1	....	......	....	0.05	0.2^{1}	0.2	8
6	Nil	0.04^{2}	0.02	0.1	....	......	0.4^{2}	0.3^{4}	0.5	2	6
7	Nil	0.3^{3}	0.2	0.9	....	......	2	$1^{2,3}$	6^{3}	2	7
8	0.0002	0.009	0.003	0.03	0.001	0.006	0.004	....	0.3	0.09	4
9	0.0003	0.09^{3}	0.8	1	0.001	0.2	....	....	6	1	14^{1}
10	0.0002	0.1	0.3	0.4	0.01	0.01	$0.2^{1,4}$	....	2	0.8	30
11	0.002	0.003	0.03	0.05	....	......	....	0.02	0.2^{1}	0.6	3

[1] Slight or shallow pitting attack.

[2] Moderate pitting attack.

[3] Severe pitting attack.

[4] Slight attack under spacer.

[5] Moderate attack under spacer.

[6] Severe attack under spacer.

[7] Specimens perforated by severe pitting attack.

Exposure No.	Environment	Temperature	Duration of Test, Days
1	Moist air containing alkaline contaminants	Ambient	166
2	Moist air containing HCl and Cl_2	Ambient	118
3	Moist air containing HCl and Cl_2	Ambient	92
4	Moist air containing HCl	Ambient	137
5	Moist air containing Cl_2	Ambient	166
6	Moist air containing traces of Cl_2	92 F	214
7	Moist air containing traces of Cl_2	98 F	214
8	Moist air containing traces of Cl_2	Ambient	195
9	Moist air containing Cl_2	Ambient	195
10	Moist air containing Cl_2	Ambient	195
11	Moist air containing Cl_2	120 F	166

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[a] Reprinted with permission from Gegner and Wilson.[157]

See, for example, the corrosion rates of mild steel in exposures 9 and 10, for where the environment is described as "moist air containing Cl_2"; one might expect the corrosion rates to be the same, but they differ considerably. Hence, it is not possible to draw any conclusions regarding the data presented. It is of interest, however, that the corrosion rates are much greater than those presented in the Wyandotte study.[172]

No significant data on the corrosiveness of hydrogen chloride in the environment appear to be available (the same conclusion has been arrived at elsewhere[447]). We find that interest has centered about concentrations that are found in industrial manufacture and use.[461]

No data on the corrosion rates of textiles or building materials, such as limestone, in the presence of trace quantities of atmospheric chlorine or hydrogen chloride could be obtained from the literature. Nor is there any evidence to indicate whether ambient atmospheric concentrations of chlorine have a bleaching effect on textiles.

AGGRAVATED CORROSION

Aggravated corrosion is defined as the corrosion that occurs when there is a major release of, say, chlorine or hydrogen chloride and the concentrations substantially exceed those which might prevail over an extended period in the neighborhood of an emission source. Because these events are rare and brief, it follows that materials will be exposed to accelerated corrosive attack only rarely and for very brief periods. Consequently, data obtained from long-term exposures are not useful.

The concentration of any gas emitted from a point source at a given rate is calculable.[229] However, the effects on materials of brief exposures to chlorine or hydrogen chloride are not known. One observation has been made regarding property damage after a train derailment in which a chlorine car was ruptured: "Farm implements and tools were badly corroded and rusted wherever they were exposed, particularly where dew had condensed on the surface."[416 (p. 21)] One would expect a similar result from a release of hydrogen chloride.

OBNOXIOUS ODORS

The mere definition of what constitutes an obnoxious odor is a formidable task. To be sure, there will be total agreement on whether some specific odors are obnoxious--for example, a strong odor of putrefying meat. The difficulty arises when there is an attempt to set some sort of threshold above which an odor is obnoxious. The reason is that the only means of identifying an odor as obnoxious is the capricious human sense of smell. Furthermore, individual sensitivities, odor fatigue, weather conditions, and other factors complicate matters.[388]

The olfactory threshold of chlorine and hydrogen chloride is discussed in Chapter 5, and no details will be given here. However, it might be pointed out that the olfactory threshold is often used as the criterion for identifying an odor as obnoxious. Rjazanov goes further in considering subsensory effects (such as changes in nervous activity) in labeling odors as obnoxious.[395] It is not clear whether he used this criterion in the case of chlorine and hydrogen chloride, but he does recommend the very low atmospheric chlorine and hydrogen chloride concentrations of 0.03 mg/m^3 and 0.015 mg/m^3, respectively, as the maximal allowable exposure limits, averaged over a 24-hr period, for the general public.

Chlorine manufacturing plants have a characteristic odor that those who are experienced will identify as being not due to chlorine. The odor is not nearly as acrid as that of chlorine and is similar to the odor usually associated with organic compounds.

In the manufacture of chlorine, small amounts of low-volatility chlorinated organic compounds are produced by the reaction of chlorine with graphite anodes and organic-based materials of construction, sealants, and the like. During operation of the plant, some of these chlorinated organic compounds are deposited in pipelines and processing equipment. When they are opened to the atmosphere for cleaning or maintenance, some of the compounds escape and, because of their low volatility, linger in the area and impart their characteristic odor to the atmosphere. This hypothesis is at least partially borne out by the fact that a new plant, on starting up, does not have the characteristic odor, but develops it after the first maintenance or cleaning operation.

The low-volatility organic compounds have been identified as polychlorinated aromatic and aliphatic compounds, such as pentachlorobenzene, hexachlorobenzene, hexachloroethane, and hexachlorobutadiene. There may also be opportunity for chlorine to react with ammonium compounds or amines present in rainwater, process cooling water, etc. In such cases, formation of monochloramine, dichloramine, and nitrogen trichloride might occur, although it has not been established. These also have a characteristic odor that differs from that of chlorine.

DISCOMFORT

Actual discomfort among the general population near chlorine and hydrogen chloride emission sources will not occur under normal operating conditions. Only when atmospheric concentrations are moderate or high because of accidental releases of chlorine and hydrogen chloride will this potential exist. The threshold concentrations for human discomfort and accompanying symptoms are discussed in Chapter 5.

The chlorinated organic derivatives just discussed are highly unlikely to produce any discomfort among the general population. In fact, because of the minute quantities involved, it is probably safe to assert that such an occurrence is impossible.

The chloramines and nitrogen trichloride can be rather irritating in sufficiently high concentrations, although these concentrations are unknown. If they are generated on the premises of chlorine plants, the amounts would be too small to constitute a potential irritant to the public.

TRAFFIC AND NAVIGATIONAL HAZARDS

It is well known that traffic and navigational hazards may be caused by mist and smog, which are at least partially caused by the presence of pollutants that act as nuclei for the coalescence of water vapor. There is no evidence in the literature that chlorine or hydrogen chloride has been specifically identified as being at fault in this respect. It is likely, however, that they contribute, where present, with other chemical pollutants. At what concentration this contribution is significant is unknown.

When substantial amounts of hydrogen chloride are released into the atmosphere, a white mist or cloud results from reaction with atmospheric water vapor. Under appropriate meteorologic conditions, such a hydrochloric acid cloud can be sufficiently opaque as to impede traffic and interfere with navigation. No account of such an event has been found in the literature. Industrial sources have indicated that such events occasionally occur, although their frequency is not known.

Another type of haze is associated with the reaction of ammonia with hydrogen chloride or chlorine in the atmosphere. The acid gases react with the alkaline ammonia to form ammonium chloride salt, which sublimes to a white powder. Such a phenomenon can occur where chlorine or hydrogen chloride and ammonia are manufactured or used in proximity. Again, it is known from industrial sources that this occurs occasionally, but the frequency is not known, nor has any mention of it been found in the literature. It should also be noted that a similar phenomenon can occur with the reaction, for example, of ammonia, water vapor, and sulfur dioxide to form ammonium sulfite.

The haze formed by the reaction of ammonia with an acid gas has a potential for producing a navagational hazard or impeding traffic movement by lowering visibility. The haze may be white or blue, depending probably on particle size, angle of light incidence, and viewing angle.

CHAPTER 8

SAFETY IN USE AND HANDLING OF CHLORINE AND ANHYDROUS HYDROGEN CHLORIDE

CHLORINE MANUFACTURE

Safety in the manufacture of chlorine has been a prime consideration since the inception of the chlorine industry in the late nineteenth century. Developments in processes and controls, in the handling of chlorine gas and liquid, in the minimization of potentially dangerous impurities, and in the packaging and transportation of liquid chlorine have enabled the industry to produce and distribute thousands of tons of chlorine each day in the United States.

Before a discussion of the various aspects of manufacturing safety, it is pertinent to summarize the most common chlorine manufacturing processes and the properties of chlorine.

The majority of chlorine is produced by the electrolysis of sodium chloride or potassium chloride brine solution; small quantities are produced by the electrolysis of molten salt or hydrochloric acid. Only the electrolysis of brine will be treated here.

Wet chlorine gas is produced directly by the electrolysis cells, with byproduct sodium hydroxide and hydrogen gas produced either directly (in diaphragm cells) or indirectly (in mercury or amalgam cells). The wet chlorine gas is continuously removed from the cells by the partial vacuum created by chlorine compressors. It is pulled through demisters to remove entrained salt, pulled through indirect- or direct-contact coolers to reduce temperature and water content, and dried with concentrated sulfuric acid in packed towers. In some installations, the dried chlorine gas is further purified and cooled before compression by scrubbing the gas with liquid chlorine reflux in a packed tower.

Several types of chlorine compressor systems are used. The most common are rotary compressors that use concentrated sulfuric acid as a seal liquor and large multi-stage centrifugal compressors. After compression to 35-150 psig (it varies in different installations), the gas is transferred directly to processes that use gaseous chlorine or is cooled to 20^{o} F (about 6.7 C) or below in liquefiers to form liquid chlorine, which is then transferred to pressurized tanks, where it is stored as a liquid until used or loaded for shipment. Tail gases from the chlorine liquefier, containing up to 50% gaseous chlorine and noncondensable substances--such as hydrogen, nitrogen, oxygen, and carbon dioxide--are processed by various means, either to produce chlorinated products or to recover chlorine from the stream.

Chlorine at ordinary temperatures and pressures is a greenish-yellow gas with a pungent and irritating odor. When diluted in air, chlorine can be undetectable by sight, and its color cannot be used as a guide to its concentration. Because of its reactivity, chlorine is found in nature only in combination with other elements. Gaseous chlorine is approximately 2.5 times as heavy as air, so leaked chlorine tends to accumulate in the lowest part of a building or area. Liquid chlorine is clear, amber in color, and about 1.5 times as heavy as water. At atmospheric pressure, chlorine boils at about -30 F (about -34.4 C) and freezes at about -150 F (about -101.1 C).

Chlorine's characteristic odor can be detected at a concentration of approximately 0.3 ppm in air. Neither liquid nor gaseous chlorine is flammable or explosive, but gaseous chlorine will support the combustion of some materials under special conditions. Chlorine is an excellent oxidizing agent and is very active chemically with many substances. Although dry chlorine does not react with many metals, it is very reactive in the presence of moisture.

Materials of Construction

Wet chlorine attacks most common metals, so rubber-lined, brick-lined, glass, or ceramic equipment is often used in chlorine plants. Acid-resistant polyester or phenolic-based resins are used predominantly for pipe construction in wet-gas systems, with polyvinylchloride (PVC) and polyvinyldichloride (CPVC) also used for smaller-diameter piping. Titanium is used for wet-chlorine equipment, particularly for heat exchangers and low-pressure blowers. (Dry chlorine, however, readily attacks and can spontaneously ignite titanium). Tantalum, platinum, gold, and silver are also resistant to wet-chlorine attack.

Dry chlorine gas and liquid (moisture less than 150 ppm by weight) are normally handled in iron or steel equipment and piping. Some stainless steels, nickel, copper, Monel, brass, bronze, tantalum, and lead can also be used for dry chlorine. Introduction of moisture will cause severe corrosion of these metals (except for tantalum), so strict monitoring and control of moisture in the process are of utmost importance in the handling of dry chlorine.

Overpressure Relief and Emergency Vents

In chlorine manufacturing plants, chlorine is handled at pressures up to 250 psig. Safe handling and chlorine emission control dictate the need for overpressure protection and containment or neutralization of process gas streams.

Primary overpressure protection for the electrolytic cells and the cell-room chlorine piping system consists of a water seal. This seal is often a combination pressure and vacuum seal, with air pulled in to avoid high vacuum in the cells, or chlorine gas directed to a caustic scrubbing system in the event of excessive header pressure. Other designs incorporate a separate header system in the cell room to divert cell gas to a caustic scrubber if pressure on the cells exceeds several inches of water.

Water seals at the individual cells or the main chlorine header separate the main chlorine collection piping from the weak gas header.

Pressure vessels are protected from overpressure by rupture disks or relief valves set to relieve at code-approved pressures. Silver, tantalum, or impervious graphite rupture disks are generally specified. Spring-loaded relief valves like those on chlorine tank cars are the most commonly used.

On pipelines conveying liquid chlorine, expansion chambers are used to prevent overpressure from thermal expansion in the line. Often, 1-ton containers or chlorine cylinders are adapted for use as expansion chambers.

Properly instrumented power-operated control valves are often used, rather than check valves, in pipelines. Rising-ball check valves, used in chlorine tank cars and storage tanks, are designed to check when excessive flow occurs. Spring-operated swing check valves have been used for discharge piping from chlorine compressors.

During plant startup and shutdown and during process upsets, emergency vent systems are used to prevent release of chlorine gas to the atmosphere. Various designs are used for emergency vent systems, but all include piping and equipment for the neutralization of chlorine gas in a caustic soda solution. Piping and valves are designed to permit alternate routing of chlorine gas from various points in the process directly to the emergency vent system. Remotely operated valves are often used. To neutralize the chlorine gas, weak caustic soda is used to react with chlorine; this forms hypochlorite, and chlorates, and only the inert gases are vented.

The caustic is generally circulated through a packed tower or contained in a sparger tank, where it contacts and reacts with the chlorine,releasing only inert gases to the atmosphere.

Hydrogen Explosions

In the electrolysis of brine solutions, gaseous hydrogen is also produced in the cell gas, usually in concentrations below 1%. Because chlorine and high-concentration hydrogen can form explosive mixtures, prevention and control of excessive hydrogen generation in the cells is a major concern in chlorine manufacture.

Prevention of excessive hydrogen generation is based primarily on brine purity and proper cell operation. Metallic impurities in brine catalyze hydrogen generation in electrolytic cells; therefore, brine purification systems are designed to reduce metallic impurities. Proper pH adjustment and control, carbonation of the brine with soda ash or carbon dioxide, and clarification and filtration are used to control brine purity. The brine is analyzed routinely to monitor brine quality.

Proper cell operation depends on operator and instrument monitoring of cell variables. Periodic analyses of cell gas are run on individual cells and on the main chlorine pipeline to determine hydrogen content of the cell gas. Often, hydrogen in the main cell gas stream is monitored continuously. Backup analyses are routinely run on the compressed chlorine and tail gas to provide further control.

In diaphragm cells, the amount of brine in the cells and the caustic flow from the cathode are monitored. In mercury cells, individual cell voltages and mercury are also monitored. The proper mix of trained operators and modern control equipment are used to control both brine purification and cell operation to minimize hydrogen generation in the cells.

Occasionally, excessive hydrogen is generated, because of a process upset. The response varies according to the individual circumstances, but consists of:

- Immediate addition of air at the cells, after compression and after liquefaction to bring the hydrogen content in both cell gas and tail gas below potentially explosive limits.
- If required, reduction of electric power to the electrolytic cells or shutdown of the cell circuit to keep the hydrogen concentration of the various streams below explosive limits (the hydrogen content in the tail gas stream is important, because the removal of a portion of the chlorine in the liquefier concentrates the hydrogen in the tail gas stream; increased hydrogen in the cell gas can be well below explosive limits while that in the tail gas is at an explosive point).
- Troubleshooting to identify and eliminate the cause of increased hydrogen generation.

If excessive hydrogen generation is due to brine quality, the brine must be treated chemically to isolate high metallic impurities and stabilize the pH to bring brine quality to normal. If the cause is a malfunction of an individual cell, the cell must be taken off line until the problem is corrected.

In rare instances, excessive hydrogen generation can result in an explosion. Hydrogen explosions generally occur in individual cells, at the first-stage drying tower, in the liquefier, or in the tail gas stream.

Response to a hydrogen explosion depends on the cause, location, and severity of the explosion and is determined primarily by the requirements for personnel safety and control of chlorine release. Plant design, emergency planning, and personnel training are the keys to a safe and orderly response to explosions in a chlorine plant. Strategically placed and remotely operated valves are used to direct all process gases to the emergency vent system immediately, to minimize chlorine release to the atmosphere.

Remote cell-circuit trip switches, automatic compressor controls, and so forth are incorporated into plant design specifically for emergency situations.

Emergency planning and personnel training geared to specific emergency situations ensure that the proper response to an upset condition will be taken. The emergency plan assigns responsibility to groups and individuals in the plant for each of the critical activities that must be undertaken immediately, to minimize atmospheric releases, protect plant personnel and people in the vicinity, and secure the plant after an explosion. The following are the most critical functions:

- Donning of adequate respiratory protective equipment by plant personnel.
- Accounting for all plant personnel.
- Removal of injured persons exposed to chlorine to safe areas and administration of first aid as required.
- Diversion of process gas streams to the emergency vent system.
- Shutdown of cell circuits to stop further production of chlorine.
- Isolation of damaged equipment to prevent further chlorine release.
- Assessment of extent of chlorine release to the atmosphere.
- Notification of local authorities and neighboring industry to apprise them of the situation and to initiate coordinated area emergency plan.
- Evacuation of affected area, if necessary.
- Securing of plant equipment.

These functions, undertaken essentially simultaneously, apply to a severe explosion in a critical pipeline or process vessel. An explosion in an individual cell or in the tail gas system would usually be met by isolating only that cell or part of the plant.

Chlorine plant hydrogen explosions are rare. Therefore, emergency planning must include continual training, emergency drills, formal review of responses to specific upset conditions, and retraining. The emergency plan should be coordinated in advance with an area emergency plan or with the appropriate local authorities and nearby industries for assistance and protection of people in the area.

Nitrogen Trichloride Explosions

Ammonia can combine with chlorine to form nitrogen trichloride, NCl_3. Nitrogen trichloride is a yellow, oily liquid that is soluble in all proportions with liquid chlorine. It is a highly explosive compound and, when isolated, will detonate spontaneously at temperatures above 55-95 C (depending on air concentration).

In some areas of the United States, the salt deposits used for chlorine production contain ammonium compounds. The brines produced from this salt can be treated with small amounts of chlorine gas and air-blown to reduce the ammonia content before use in the chlorine cells. At least one plant in the United States has used ultraviolet radiation of the cell-gas stream to reduce nitrogen trichloride to chlorine and nitrogen.

A significant point of nitrogen trichloride removal in many plants is the chlorine purification tower, where liquid chlorine is used to cool and reflux the main cell-gas stream in a packed tower. Nitrogen trichloride accumulates in the residue, or "bottoms," of the purification column, where it is diluted with an inert organic solvent. In solution, nitrogen trichloride is safe to remove from the column on a regular basis.

Another significant factor in the reduction of nitrogen trichloride to chlorine is the heat produced by chlorine compression. In a chlorine-nitrogen trichloride system, temperatures above 50 C promote decomposition of nitrogen trichloride to chlorine and nitrogen, especially in the presence of iron compounds.

Control of nitrogen trichloride and avoidance of nitrogen trichloride explosions, therefore, depend on a variety of factors. Regular analysis for nitrogen trichloride in the cell-gas stream, liquid chlorine production, and purification bottoms is essential. Depending on plant design, a combination of removal schemes can be used to reduce nitrogen trichloride to a safe concentration.

The chlorine purification column, which removes nitrogen trichloride, is the most vulnerable location for a nitrogen trichloride explosion in a chlorine plant, particularly during an extended plant shutdown. During a shutdown, the liquid chlorine in the column will be vaporized and removed, and the vessel temperature will increase. The nitrogen trichloride, harmless while at low temperature and diluted in chlorine, will become concentrated unless other dilution is used. Thorough rinsing of the column and piping is therefore done during plant shutdowns to remove and dilute nitrogen trichloride.

Nitrogen trichloride explosions are most likely to occur during a shutdown of the plant, so response consists primarily of handling injuries to personnel and damage to equipment caused by the explosion. Other equipment that could be the site of a similar explosion should be immediately secured by dilution. The cause of the nitrogen trichloride buildup must be found and eliminated, to prevent future explosions.

Corrosion-Induced Pipeline and Vessel Failures

After drying, chlorine is handled in an all-steel system--steel piping, compressors, and vessels. The introduction of any moisture into the system can accelerate corrosion of the steel to the point of failure. In extreme cases, the moisture in the all-steel system can promote spontaneous combustion of the chlorine (chlorine "fires"). Therefore, corrosion control in chlorine handling systems depends on moisture control.

The chlorine gas is passed through a series of packed towers countercurrent with concentrated sulfuric acid for drying. The relative dryness of the chlorine gas stream is controlled by the acid concentration in the last-stage drying tower. Virgin concentrated acid is added at such a rate as to keep the last-stage acid concentration above the minimum that will yield dry chlorine gas containing water vapor at less than 150 ppm. When acid flow in the drying towers is interrupted, the cell circuit must be shut down to prevent moist chlorine from passing through the drying towers to the steel equipment. The drying towers must be kept in proper operation at all times, and the gas stream must be analyzed periodically or continuously for moisture, to verify proper operation.

Addition of air to the chlorine stream is another possible source of moisture. Automatic regenerative air driers capable of keeping moisture content below 100 ppm in the air (dew point, -40 C) are used on compressed-air systems in a chlorine plant. Dryness is monitored through periodic analyses run on the exit air from the driers.

Regular inspections of piping and equipment in chlorine service are essential in preventing corrosion-induced failures. Sonic and x-ray testing are also used on critical equipment and piping, to ensure integrity of the welds and steel.

Hydrostatic testing of new or repaired piping systems and equipment is standard procedure in chlorine plants. After the hydrostatic test, the equipment must be dried with steam and then purged with dry air. Process and storage vessels are hydrostatically tested regularly.

Fail-Safe Compression Systems

The main chlorine compression system is the integral part of a chlorine plant, with regard to control of chlorine emission to the atmosphere. The cells are continuously producing chlorine, and the compression system must remove the gas from the cells, compress it, and pump it through liquefaction to storage. Various compression systems are used for chlorine: rotary compressors with a sulfuric acid seal medium, multistage centrifugal compressors, and reciprocating compressors. Rotary and centrifugal compressors are predominant; centrifugal compressors are preferred in the newer plants. The compression systems are designed to maintain a slight vacuum on each electrolytic cell, to pull the gas through the cooling and drying steps to the compressor suction. Compressor discharge pressures vary from 35 to 150 psig. Fail-safe design implies that no chlorine gas will be emitted under any circumstance--compressor shutdown, power outage, power surge, or other equipment or piping failure. This has not been fully achieved for all contingencies, but compressor system design includes many features that allow fail-safe operation to be approached.

The most difficult situations to provide fail-safe compression systems for are complete power outages (assuming an electrically driven compressor), compressor tripoffs, and cell circuit tripoffs. In a complete power outage, all additional chlorine production from the cells stops, but chlorine gas in the system must be removed and there must be adequate provision to prevent the chlorine pressure at the compressor discharge from backing into the chlorine suction header, drying towers, and cell room. In the case of a compressor tripoff, the cells continue to produce chlorine gas, and system chlorine pressure can back into the cell room, as in a complete outage. In a cell circuit tripoff, the ceasing of chlorine gas production can create compressor control difficulties. If sufficient air is drawn into the system before the compressor recycle control responds, a centrifugal compressor can go into surge and stop pumping.

The plant design must minimize the potential for chlorine release to the atmosphere for these extreme cases. The following describes several features that are included in some plant compression designs. It is not intended to imply that all plants incorporate these features or that other approaches to fail-safe compression systems are not being used.

Automatic suction control in some systems includes butterfly-valve control of the suction on the main chlorine header, in addition to compressor recycle control. Such a system provides relatively independent cell-room suction control, with the compressor operation controlled by the recycle of gas from the discharge back to the suction. When a large change occurs in the amount of chlorine being handled (owing to a power surge or a cell circuit shutdown, for example), the compressor recycle operates to keep the compressor loading constant. The butterfly valve on the main chlorine header adjusts to the changing pressure drop through the piping and equipment from the cell room to the compressor suction, to maintain a constant negative pressure on the cell circuit. Wide-range control with this system has been difficult to achieve, however, so the pressure-vacuum seal or weak-gas header system is used to back up the suction controller.

The pressure-vacuum seal system, as described earlier, either pulls air into the system to prevent excessive negative pressure on the cells or diverts excessive gas to the caustic scrubber to relieve pressure. On pressure relief, the gases are conveyed to a nearby scrubber tower for neutralization with caustic soda. Other designs incorporate an auxiliary header in the cell room. This auxiliary piping conveys chlorine gas directly to a caustic scrubber system and in this manner relieves pressure on the main chlorine header.

Some plant designs include interlocking relays between the main chlorine compressor and the cell circuit; if the compressor trips off, the cell circuit is automatically tripped off, also. This has not gained wide acceptance, because of startup difficulties with the interlocking system and because many plants use multicompressor systems, which obviate interlocks. Compressor reliability has been outstanding in the chlorine industry, with continous operation for a year or more not unusual.

There have been several approaches to the problem of compressor discharge pressure that backs into the cell-room chlorine header during compressor shutdown or complete power outage. Spring-loaded swing check valves on the compressor discharge have given satisfactory service in some plants; in other locations, their reliability is suspect. Three-way, air-operated ball valves have been used to isolate the compressor discharge to the emergency vent system. Remotely operated valves on the main chlorine suction header are also used to divert this stream to the emergency vent system.

Thus, there is a basis for compression system designs that approach fail-safe in a chlorine plant. Some situations, particularly those involving equipment failure or malfunction, will cause some release of chlorine to the atmosphere; the basic design elements discussed here will minimize such releases.

Compressor Fires

Chlorine "fires" with steel are self-sustaining chemical reactions between chlorine and steel, accompanied by a high heat of reaction. Chlorine fires in a steel chlorine compressor can be caused by moisture in the chlorine gas or sulfuric acid seal liquid (with a rotary compressor), localized high temperatures from friction of moving parts or excessive gas temperature, and oil or other organic contaminants.

Moisture exclusion from the chlorine gas and air systems was discussed earlier, and the same factors apply to compressors. In addition, where rotary compressors are used, concentrated sulfuric acid is the seal liquid in the compressors. Sulfuric acid strength must be monitored and virgin acid added, to keep acid strength high enough to avoid a weak sulfuric acid reaction with steel. Sulfuric acid below a concentration of approximately 70% is very corrosive to steel, and a byproduct of the corrosion reaction is hydrogen gas, which presents a fire and explosion hazard.

The reactivity of chlorine with such organic substances as oil can contribute to a fire potential in a compressor. Chlorine compressors should be designed to isolate the lubricated bearings via air purged or open distance pieces or chambers to prevent oil from entering the compressor. Valves and compressor parts are disassembled and washed in an inert organic solvent before they are put into use, so as to remove traces of machine oils. Because chlorine can be very reactive with many organic compounds, the inert solvent should be a chlorinated hydrocarbon, such as perchloroethylene.

In the design of chlorine compressors, particularly high-speed centrifugal compressors, consideration must be given to the effects of heat from the friction of moving parts. A detailed discussion of chlorine compressor design is beyond the scope of this report, but accurate maintenance of metal-to-metal clearances, the use of nonmetallic surfaces, and labyrinth seals between compressor stages are incorporated into the machine design to prevent localized high temperatures.

In multistage compressors, integral compressor-housing cooling jackets or auxiliary coolers between stages are needed to control the temperature of compressed chlorine gas. High-temperature protection includes alarm devices at one temperature and machine tripoff at a somewhat higher temperature, with maximal operating temperature generally limited to about 300 F (150 C). Coolers are designed for low-pressure discharge of the cooling medium (water or chlorinated solvent), to prevent the cooling medium from entering the gas stream. The cooling water is monitored regularly for evidence of cooler leak.

If a compressor fire occurs, the immediate responses are to vent the machine to the emergency vent system, isolate the compressor from the system, and flood the compressor and piping with dry nitrogen gas. Because the chlorine "fire" is a self-sustained reaction, the use of nitrogen to purge residual chlorine from the machine and piping is the prime consideration in extinguishing the fire.

CHLORINE TRANSPORTATION

Containers

Chlorine is stored and shipped as a pressurized liquid in cylinders, 1-ton containers, single-unit tank cars, cargo tank trucks, and tank barges. All containers used in the transportation of chlorine are controlled by federal or other governmental regulations, and it is the responsibility of each person transporting chlorine to know and to comply with all applicable regulations. A brief summary of the design of each type container is given below.

Chlorine cylinders (capacity, 1-150 lb, or 0.45-67.5 kg) are of seamless steel and of the "foot-ring" or "bumped-bottom" type meeting Interstate Commerce Commission (ICC) or Department of Transportation specifications for chlorine service. All cylinders and 1-ton containers must be requalified by hydrostatic test every 5 years; test records must be maintained for all containers in use; and serial numbers and dates of tests must be stamped on the containers.

The only opening in a cylinder permitted by regulations is the valve connection at the top. A steel hood covers the valve. Cylinders in an upright position deliver gaseous chlorine; they may be inverted to deliver liquid. The outlet-valve design includes a fusible metal plug that melts at 158-165 F (70-74 C) for overpressure relief. Cylinders may be shipped by truck, rail, or water in truck or carload quantities or less.

One-ton containers are welded tanks 30-in. (76.2 cm) in diameter that meet ICC specifications for chlorine containers. The container is equipped with two identical valves at one end; each valve is connected to an internal eduction pipe. The eduction pipes are so arranged that, when the container valves are vertical, gaseous chlorine will be delivered from the upper valve and liquid from the lower valve. Most containers have six fusible plugs (three at each end) that are designed to melt at 70-74 C for overpressure relief. The heads of the container are convex inward, with the sides crimped inward to provide chimes for lifting the container. The valves are protected by steel hoods. One-ton containers may be shipped in lots of 15 by rail (multiunit tank cars) and by truck or water.

Single-unit chlorine tank cars are built according to ICC regulations in capacities of 16, 30, 55, 85, and 90 tons. They are insulated to minimize temperature and pressure buildup in transit and during storage and are designed for unloading liquid chlorine directly to the user's vaporizing equipment or process. The only openings in a tank car are at the dome, where five valves are mounted within a protective hood. Two of the valves are connected to internal eduction pipes for liquid chlorine withdrawal; ball check valves are installed under the liquid valves to interrupt flow if the withdrawal rate exceeds rated capacity. Two valves are mounted directly on the dome and are used for adding dry air or nitrogen to the vapor space to increase liquid removal rates. These valves are also used for depressuring and evacuating the tank in the loading plant. The fifth valve, mounted in the center of the valve cluster, is a safety relief valve set to operate when the pressure in the car reaches 75% of test pressure.

Cargo tank trucks with capacities of 15-20 tons are also used. The dome and valve arrangements are identical with those of tank cars, except that excess-flow valves are also required under the gas valves. Tank trucks are also insulated.

Chlorine barges are of the open-hopper, double-skin type, with a number of cylindrical tanks mounted horizontally. Different configurations in capacities up to 1,100 tons are in use and are regulated by the U.S. Coast Guard. All openings in a barge tank are required to be in the top. Unlike those in tank cars and trucks, valve arrangements are not uniform. Depending on the capacity of the individual tank, two or three safety valves rated at 300 psig are used on each tank (each barge has four tanks), with a variable number of operating valves. Under each liquid valve, excess-flow valves are installed at the top of the eduction pipe. Under each gas valve is a different excess-flow valve designed to close if the operating valve is broken off. All valves are enclosed in protective hoods. Underwater sonic-detection devices are installed on chlorine barges to aid in locating them if they sink.

Proper handling of chlorine containers is essential in transportation. Cylinders and 1-ton containers must be secured rigidly to prevent falling. Cylinders should be transported and stored in an upright position and 1-ton containers should be transported on their sides on steel supports. Valve-protection hoods must be securely in place during movement of all containers.

Exposure of containers to flame, intense radiant heat or high temperature of any source is to be avoided. Fusible plugs in small containers will melt at around 70 C, and excessive chlorine vapor pressure due to increased temperature in tank cars, trucks, or barges will cause the safety valves to operate. Intense local heat on the steel containers will increase corrosion on the steel walls, and the steel will ignite at high temperatures (420-500°F, or 215-260 C, depending on surface conditions, impurities, etc.). Response to fires in transit consists of immediate removal of chlorine containers from the fire zone. If no chlorine is escaping, water should be applied to the containers to cool them, if they cannot be moved. If chlorine is being released, water should not be sprayed directly on the leak, because that would increase the leakage rate.

If a chlorine leak develops in transit, usually the best practice is to continue moving the container until it is out of a populated area. Properly trained personnel with protective equipment should then be dispatched to secure the leak. If necessary, the affected area should be evacuated. Emergency kits have been designed to stop most leaks that may be encountered in chlorine containers. Three standard emergency kits sold through the Chlorine Institute, Inc., are designed for cylinders, 1-ton containers, and tank cars and tank trucks. Because barge tank design is not uniform, kits designed for specific barges are on board or at barge loading plants. Producers, repackagers, and many users of chlorine maintain emergency kits and trained teams experienced in their use. Motor vehicles that are used to transport chlorine containers are required to have appropriate emergency kits on hand. The following general rules apply to most chlorine-container leaks:

- If possible, turn container so that gas, rather than liquid chlorine, escapes. One volume of liquid chlorine is equivalent to about 460 volumes of gas.

- It is often advisable to move the container to an isolated area where it will do the least harm.
- If it is practical, reduce pressure in the container by removing chlorine as a gas to a user's process or disposal system. The vaporization of liquid chlorine in the container will cool the remaining liquid, reducing the container pressure and the magnitude of the leakage.
- Apply an emergency device to stop leakage.

In the event of a wreck where chlorine is leaking, the affected area should be evacuated and emergency assistance obtained. Trained emergency teams are available around the clock from any chlorine-producing plant.

The Chlorine Institute has initiated CHLOREP, a 24-hr/day emergency assistance program for the entire United States. A call to a chlorine producer or repacker or directly to CHLOREP will bring trained emergency teams with suitable emergency equipment to the scene of a chlorine incident. On arrival at the scene, the CHLOREP team, with support personnel in telephone contact, will advise local authorities on evacuation, handling of the leaking container, securing of the leak, and arrangements for removing damaged containers.

Of course, the first concern in the event of a chlorine leak should be the protection of people. All people downwind of a chlorine leak should be removed from the area. In the case of actual or potential large-scale chlorine releases, meteorologic estimation of the atmospheric dispersion of the release may be required for determining evacuation areas. Only trained personnel with suitable respiratory protection should approach the leaking container to move it or to secure the leak. Persons who inhale chlorine should be removed to a safe area and given first aid, and emergency assistance should be sought as soon as possible.

Pipelines

Steel pipelines for both gaseous and liquid chlorine are used by the U.S. chlorine industry for interplant transfer and customer delivery of chlorine in some locations. The distances involved have been relatively short, with design of the piping systems providing a high factor of reliability.

Chlorine pipeline systems have been installed both below and above ground. Design considerations for the system include providing protection from traffic and from heavy equipment. Below grade, encasement of the piping at crossings and cathodic protection must be provided.

Chlorine pipelines are of welded carbon steel with flanged valves. Expansion loops are used, rather than expansion joints, and there is access to the line for cleanout, washout, and hydrostatic testing.

Expansion tanks are provided for potentially isolated sections of the line, and there are also pipeline depressurization and evacuation facilities. The depressurization facilities usually include an evacuated tank and automatic or semiautomatic controls for rapidly dumping the line pressure and contents into the tank in case of a pipeline leak.

Proper operation and maintenance of a chlorine pipeline include the general equipment and piping practices discussed earlier. Particular care must be taken in the construction, repair, and drying of the pipeline. Hydrostatic testing after repairs or modification of the line and at regular intervals ensures the integrity of the pipeline. X-ray examination of welds is also used.

Regular inspection of the external condition of the pipeline and inspection and testing of cathodic protection systems are essential for safe pipeline operation. Any deficiencies on the piping, cathodic protection system, or support structures should be promptly corrected.

Emergency procedures for leaks should be drawn up and personnel at both ends of the pipeline should be well trained in these procedures. Dry-run emergency drills, actual pipeline evacuation drills, and formal review of procedures are integral parts of the emergency plan.

Response to a pipeline leak will consist of shutting off chlorine feed to the line, dumping of the pipeline contents into an evacuated vessel, notification of emergency teams at both ends of the pipeline, and notification of local authorities and industries. The disaster team will immediately don respiratory protective equipment and assess the impact of the chlorine emission from the line. If necessary, the affected area will be evacuated. In general, the response to a pipeline leak will be dictated by the needs to protect people and to minimize chlorine emission.

CHLORINE CONSUMPTION

Chlorine is commercially used in many varied processes ranging from a few pounds per day, as in small water-treatment plants, to several hundred tons per day, as in pulp and paper bleaching or organic chlorination plants. As discussed earlier, safe use of chlorine depends on proper equipment design, materials of construction, employee training, and emergency planning. Chlorine is received in cylinders, 1-ton containers, tank cars, tank trucks, and barges or via pipeline. Although most users store the chlorine in those containers, some barge and tank truck users may require on-site storage tanks. There are specific requirements for use of the various containers, but general guidelines for safe chlorine handling will be discussed here.

Materials of Construction

All chlorine commercially shipped has been dried, so steel is the predominant construction material for piping and vessels in a chlorine-consuming plant. Copper or Monel is often used for flexible connections to the containers, and tantalum, graphite, lead, and silver have been used for the parts of instruments or rupture disks that contact chlorine. Both asbestos and lead gaskets are used.

Where moisture may be introduced into the process, PVC, CPVC, ABS (acryon-butadiene-polystyrene copolymer resin), polyester, phenolic-based resin, Kynar,* and rubber-lined steel may be used for chlorine gas service. Kynar has been successfully used where liquid chlorine must be introduced into a water-containing process.

Proper material selection is important in safe chlorine handling, and specific questions should be directed to the chlorine producer or to the Chlorine Institute.

Corrosion Control

As in a manufacturing plant, control of corrosion of metal equipment in a chlorine-using facility depends primarily on exclusion of moisture from the system. Dry chlorine gas or liquid is noncorrosive to most metals, but the addition of small amounts of water to the chlorine will accelerate corrosion.

Air systems used in conjunction with chlorine must be designed and operated at a -40 C dew point or below. Adequate protection from chlorine flowing back into the air drying system must be provided, lest the chlorine deactivate the desiccant. Air systems used exclusively for the chlorine system are recommended, to prevent the possibility that other uses of air in the plant will pull the air system pressure below the chlorine pressure. Multiple check valves should be installed between the chlorine and air systems and cleaned regularly with inert solvent.

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*A Pennwalt fluorocarbon resin.

Blowers and compressors used for chlorine must be designed to prevent water, moisture from the air, and oil from entering the chlorine system.

Piping and equipment used for chlorine should be hydrostatically tested after maintenance and periodically. There should be regular external inspection of the chlorine systems, and deficiencies should be corrected immediately.

Barometric loops should be installed where moisture may be sucked back into the process or container. All pipelines and vessels that are opened should be plugged off immediately, to keep atmospheric moisture from entering and causing corrosion. No flame, welding, or other heat source should be applied to a chlorine-containing vessel or pipeline before it is purged and washed.

A further consideration in corrosion control in chlorine-consuming plants is attack by liquid chlorine on many plastics, including PVC, CPVC, and ABS. Where liquid may contact moisture in the process, Kynar pipe should be used for the liquid-chlorine piping. The attack of plastic pipe by liquid chlorine is caused by solvent attack of the plasticizer or lubricant used in pipe extrusion or molding by the chlorine.

Chlorine Unloading

Specific recommendations for the design and operation of a chlorine unloading station should be obtained from the chlorine supplier or the Chlorine Institute. However, it is pertinent to summarize general guidelines for safe chlorine unloading.

Small Containers. At the point where a chlorine cylinder is to be used, a special rack must be provided to which the cylinder may be secured by chains or clamps. If gaseous chlorine is to be removed, the rack must be designed to hold the cylinder upright; if liquid chlorine, the rack must support the cylinder on its shoulder and hold it at a 60-deg angle (from horizontal). Cylinders should be moved and handled with a hand truck, and a cradle must be used to hoist them safely.

One-ton containers must be used in a horizontal position and be firmly chocked to prevent movement when in use. The two outlet valves are arranged vertically; gaseous chlorine may be withdrawn from the upper valve, liquid chlorine from the lower. Hoisting of 1-ton containers is done with specially designed lifting hooks that clamp into the chime on each end of the container. A hoist or crane rated at 2 tons or more must be used.

Cylinders and 1-ton containers should be stored and used in well-ventilated areas and protected from heat. The valve-protection hood must be in place at all times, except when the container is secured and hooked up for use. Chlorine containers should not be stored near ether, ammonia, hydrocarbons, turpentine, or other materials that are flammable or react violently with chlorine. Containers may be stored outdoors, provided they are off the ground, to prevent moisture corrosion, and also provided that the area is secure from tampering.

The container valve must be closed each time use is discontinued and it should not be used for flow regulation or throttling.

The internal vapor pressure of chlorine in the container provides unloading pressure. Padding of cylinders or 1-ton containers is not recommended. Valves, gauges, regulators, and fittings approved for chlorine service must be used. A flexible connection, usually seamless copper tubing rated at 250 psig, is used for the connection between the container and the piping system. A trained operator should be in attendance when chlorine is being withdrawn, and the container should be secured if it is to be left unattended.

Tank Cars and Tank Trucks. Tank car unloading stations must be on private railway sidings with locked switches or derails protecting the open end of the siding at a distance of at least 50 ft (about 15 m). DOT regulations specify that a warning sign and (for nighttime unloading), a blue lantern must be in place while a tank car is being unloaded. The tank car must be chocked and the brakes set while it is connected for unloading. Chlorine cars should not be unattended while they are hooked up for unloading.

A flexible metal connection (either a copper piping loop or braided Monel or stainless-steel flexible hose) is used to connect a chlorine tank car to the permanent piping system. A remotely operated shutoff valve is recommended for chlorine piping systems to limit chlorine release in case a pipeline is broken. Expansion chambers should be used if liquid chlorine might be trapped in a pipeline.

Chlorine tank cars may be padded with dry air or nitrogen (within limitations). On request, chlorine producers will add a dry air pad when the car is loaded, to improve liquid withdrawal rates. Air pads must be limited to the maximal pressure allowed by DOT regulations, which state that the vapor pressure calculated at a liquid temperature of 105 F (about 40 C) must not exceed the safety-valve rating. Air quality must be strictly monitored to maintain the -40 C dew point or lower, and all entrained oil must be removed from the air.

Because chlorine cars are well insulated, the heat required for vaporization and withdrawal of gaseous chlorine cannot be obtained, and liquid chlorine must be withdrawn from the car. Internal excess-flow valves in the liquid chlorine eduction piping limit withdrawal rates and shut off flow if the rated withdrawal is exceeded. Excess-flow valves are designed especially to protect a chlorine tank car during transit.

Design of piping systems, operating and maintenance procedures, and materials of construction described earlier must be used in chlorine unloading systems. Tank trucks are similar in design to tank cars, and similar guidelines for unloading tank trucks apply.

Barges. Unloading of chlorine barges is regulated by the U.S. Coast Guard, and the equipment and operating procedures specified by Coast Guard regulations must be used. The Coast Guard specifies that a double-braided flexible-hose connector stamped for a bursting pressure of 1,500 psi be used and provides for regular hydrostatic testing of all piping used in chlorine barge loading and unloading. Emergency shutoff valves, respiratory protection, attendance requirements, etc., are all specified in the Coast Guard regulations.

Other Engineering Safeguards

Barometric legs or vacuum breakers must be provided to present suckback of process fluids into chlorine containers. Expansion tanks should be provided on piping to trap liquid chlorine between closed valves. If liquid chlorine is trapped in a line, it will expand because of a temperature increase and can create enough internal pressure to burst the pipe.

Remote shutoff valves should be placed at appropriate points in the unloading system and process, so that the chlorine supply can be isolated quickly to prevent further release in the event of a piping failure.

Chlorine-using plants should be designed to prevent release of chlorine in the event of a process shutdown or power outage or other utility interruption and to limit release in the event of a piping or equipment failure.

Chlorine Vaporizers

Gaseous chlorine can be withdrawn for use directly into a process from cylinders and 1-ton containers at low flow rates. However, where larger gas flow rates are required or larger containers are used, vaporizers are used to revaporize the liquid chlorine.

Details differ widely in regard to construction of vaporizers, but they all operate on the same principle. Liquid chlorine is transferred from the chlorine container to the vaporizing chamber, where heat is applied. The heat, generally from either hot water or steam, is used to boil the liquid chlorine, and vapor is continuously delivered to the process. Vaporizers operate continuously and automatically, and the container pressure is usually sufficient to deliver liquid to the vaporizer.

Vaporizer design must provide for protection against flooding, adequate vapor-liquid disengagement, and superheating of the vapor. Vaporizers are sized in excess of the peak load demanded by the process. Because vaporizers are constructed of carbon steel with steel or Monel heating coils, the maximal temperature of the heating medium cannot exceed 250 F (121 C), and appropriate pressure-relief and high-temperature alarms must be provided. Design working pressure of chlorine vaporizers is at least 250 psig, and an additional 1/8 in. (0.3 cm) of corrosion allowance must be provided.

The hazards that must be considered and provided for in the design, operation, and maintenance of chlorine vaporizers are discussed below.

Reliquefaction of chlorine gas downstream of the vaporizer must be prevented by including a superheating section in the vaporizer. Chlorine gas piping should be insulated from cold process lines and atmospheric conditions. Liquid chlorine pockets in a gas system could present an overpressure hazard after shutdown of the system.

The chlorine vaporizing system must be equipped with an overpressure relief device to protect against rupture. Code-rated rupture disks and spring-loaded relief valves similar to those used on chlorine cars have been used for vaporizers. If a spring-loaded safety valve is used in series with a frangible disk, the section between them should be equipped with a pressure alarm to warn of a leaking rupture disk. Vents from the pressure relief device should be piped away from the working area, preferably to an absorption system. A barometric loop must be provided to prevent suckback of the absorption liquid.

Because steel corrosion by chlorine will be accelerated above 300 F (150 C), there must be some provision for preventing operation above the maximal design temperature of 250 F (121 C). On steam systems, a 15-psig steam-regulating valve and a relief valve set to relieve at a steam pressure below 121 C should be used. Hot-water vaporizers should be designed with a vented water jacket to prevent overpressure, and high- and low-temperature alarms for the heating medium should be used. In vaporizer operation, liquid chlorine must not be trapped in the vaporizer when it is shut down. Shutdown procedure involves first shutting off liquid chlorine supply to the vaporizer and then maintaining heat until a rapid fall in vaporizer pressure indicates complete revaporization of the liquid. Closing the gas discharge valve of the vaporizer while maintaining the heat supply will also empty the vaporizer of liquid, with the pressure buildup in the vaporizer forcing the remaining liquid to return to the container.

If moisture is excluded, the chlorine side of the vaporizing equipment does not represent a serious corrosion problem. A corrosion inhibitor or cathodic protection for the heating medium is advisable, because water or steam may cause some corrosion. The interiors of both the water or steam and the chlorine sides of vaporizers should be regularly inspected. The vaporizer should be cleaned and hydrostatically tested periodically. Because the pressure of the heating medium will be less than the chlorine pressure in a vaporizer, a leak will admit chlorine into the steam or water. A conductivity monitor or regular monitoring of atmospheric water or condensate discharge points is used to discover evidence of internal leakage during operation.

Where practical, barometric loops are used on the chlorine gas discharge to prevent process fluids from being pulled back into the vaporizer. Power-operated control valves, automatic backpressure regulators, check valves, low-pressure controls and alarms, etc., are also used where process pressures are above atmospheric pressure. These devices must be regularly maintained and tested to ensure proper operation. The emptying or changing of chlorine containers can result in changing the chlorine supply pressure and temperature. This can result in suckback of liquid chlorine from the vaporizer to the container, possibly overfilling the container. Storage of the next used container at the same temperature as those being used and control of the supply pressure at the time of container changing will prevent backflow of chlorine. Vaporization of remaining liquid chlorine and shutoff of the gas discharge valve before changing containers are other common ways to prevent suckback. It is not advisable to use check valves in the liquid chlorine supply line, because the chlorine container acts as an expansion chamber for the vaporizer in normal operation.

No case reports of nitrogen trichloride explosions in vaporizing equipment are known. Nitrogen trichloride concentrations are monitored and kept very low by the U.S. chlorine industry. In addition, the thermal decomposition of nitrogen trichloride to nitrogen and chlorine at high temperatures and in combination with steel indicates that nitrogen trichloride will not accumulate in chlorine vaporizers. As a further precaution, the internal design of chlorine vaporizers should provide unrestricted liquid chlorine flow, to prevent any pockets where nitrogen trichloride could accumulate. Internal refluxing of chlorine in the vaporizer is prevented by the superheat sections. Liquid-gas demisters are not recommended for vaporizer design, because some refluxing by the demister could lead to an accumulation of nitrogen trichloride.

Flooding of a vaporizer with liquid chlorine and carryover of liquid chlorine into the vapor discharge line can occur if inadequate heat is supplied to the vaporizer, if the vapor demand exceeds the vaporizer capacity, or if excessive padding of the chlorine container introduces high pressure into the vaporizer. A properly sized gas control valve should be installed in the vapor discharge line from the vaporizer to prevent exceeding the vaporizer capacity. A low-temperature alarm and an automatic valve actuated by low temperature of the heating medium can also prevent flooding. Air padding* of cylinders or 1-ton containers is not recommended; tank cars may be padded with dry air or nitrogen under controlled conditions only. Specific recommendations on air padding should be obtained from the chlorine manufacturer. Generally, no air pad will be required, because the chlorine vapor pressure will be sufficient to transfer liquid chlorine from the container to the vaporizer. Producers will add air pressure to tank cars on request.

Proper maintenance procedures must be followed, to ensure safe vaporizer operation. The vaporizer must be completely purged of chlorine and washed with water before burning or welding on the vessel or piping begins. After repairs and inspection, the vessel should be retested hydrostatically, heated with steam, and then air-dried to below a -40 C dew point. All gaskets should be replaced after water is drained from the vessel. After drying, the vessel should again be tested for leaks with chlorine vapor. A cloth saturated with ammonium hydroxide is used at joints, flanges, etc., to find leaks. (A white cloud of ammonium chloride is formed when chlorine comes into contact with the ammonium hydroxide.)

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*Use of compressed air above the surface of a liquid to transfer the liquid to another vessel.

After a new installation, or when new pipes or valves are used, residual oil must be washed off first with an inert solvent, such as perchlorethylene.

There should be regular preventive maintenance and testing of safety valves, check valves, automatic controls, and alarms on chlorine vaporizer systems to ensure proper operation.

No flame or other heat source should be applied to a chlorine vessel or pipe without purging and washing, because excessive heat can spontaneously ignite the steel. All piping and equipment that is temporarily disconnected--for example, the container connecting lines--must be plugged, to prevent atmospheric moisture from entering the system and causing corrosion.

These maintenance guidelines apply to all chlorine systems, including vaporizers.

In summary, chlorine vaporizers are operated safely throughout the United States. It is imperative that those operating the vaporizers understand the operating and maintenance procedures and potential hazards involved. With proper operator training, vaporizer operation is safe, easily controlled, and relatively troublefree.

Piping Leaks

The proper design and construction of chlorine piping systems are essential, to avoid piping leaks. Seamless schedule 80 steel pipe of 3/4 in. (about 1.9 cm) or above should be used, with butt-welded or flanged joints used exclusively for 1 1/2-in. (3.8 cm) or larger sizes. Tongue-and-groove or raised-face flanges are recommended. All pipe bends must be made hot and properly stress-relieved. All valves must be of the indicating type, such as rising-stem or indicating-ball valves. Only valves and gauges approved for chlorine service should be used.

Before use, all piping systems must be cleaned thoroughly with an inert organic solvent to remove traces of oil. Valves and other equipment should be disassembled and cleaned before use. Piping systems should be hydrostatically tested to 300 psig and dried to a -40 C dew point before use. Final gas testing with dry air or nitrogen is followed by the introduction of chlorine gas.

All piping should be inspected regularly and any deficiencies noted should be promptly corrected. Periodic retesting of the piping is recommended to ensure integrity of the piping.

Exclusion of moisture from the system, as discussed before, is the most important means of avoiding piping leaks.

Response to a piping leak involves shutting off further chlorine supply, diverting the remaining pressure to neutralization facilities if available, and initiating the emergency plan to prevent chlorine inhalation.

A small leak should be corrected immediately, because chlorine leaks will always get worse. No repairs should be attempted until the piping is isolated and purged of residual chlorine.

Each facility using chlorine should develop an emergency plan that includes contingency procedures for possible chlorine releases. The details of the plan should involve minimization of the release and protection of persons in the affected area. Employee training in responding to specific release situations and proper use of respiratory protective equipment should be conducted continually.

ANHYDROUS HYDROGEN CHLORIDE MANUFACTURE

Anhydrous hydrogen chloride is a colorless, stable gas at ordinary temperature. In moist air, it produces white, corrosive fumes and is readily absorbed by water to form dilute hydrochloric acid. It has a boiling point of -121 F (-85 C) at atmospheric pressure; at 68 F (20 C), it has a vapor pressure of about 600 psig. It is handled primarily as a gas, but is also commercially distributed as a liquid under pressure.

Although hydrogen chloride is not itself flammable, its reaction with steel in the presence of moisture produces hydrogen gas. This coproduct hydrogen can present both a fire hazard and an explosion hazard.

Materials of Construction

Anhydrous hydrogen chloride gas and liquid (moisture content, below 150 ppm) are commonly handled in steel piping and equipment. Nickel-alloy materials, including some low-nickel stainless steels, can also be used.

Schedule 40 steel seamless pipe for 3 in. (7.6 cm) in diameter and larger is used for dry hydrogen chloride gas at up to 100 psig and at -15 to 350 F (-26 to 177 C). Schedule 80 pipe is used for pipe smaller than 7.6 cm. Alloy 20 gate, plug, and ball valves (rating, 150 psig) are commonly used. Monel valves can also be used.

For dry liquid hydrogen chloride, schedule 80 seamless piping systems are used for all sizes, with alloy 20 valves (rating, 600 psig). Liquid hydrogen chloride storage tanks must be constructed of a steel with good low-temperature qualities; for most storage temperatures, carbon steel is satisfactory.

If the hydrogen chloride contains moisture at above 150 ppm, then plastic or rubber lining or special alloys that are suitable for hydrochloric acid must be used for equipment and piping.

Corrosion Control

In the presence of moisture, hydrogen chloride gas and liquid are very corrosive to almost all metals. Control of internal corrosion is therefore based primarily on proper design of equipment, operating procedures, and maintenance techniques to exclude moisture from the system.

Because anhydrous hydrogen chloride is extremely soluble in water and other liquids, piping design must provide barometric loops or vacuum breakers to prevent suckback into piping and containers from the point of introduction of the hydrogen chloride. Other details to exclude moisture from specific equipment must also be considered. Air systems used in conjunction with hydrogen chloride handling equipment must be operated at a -40 C dew point (for moisture at 100 ppm) or below.

Proper maintenance procedures include complete purging of piping and equipment with dry air or nitrogen before work or burning on the equipment and capping of all openings on disconnected equipment and piping to keep moisture in the air from combining with residual hydrogen chloride and forming corrosive hydrochloric acid.

To prevent hydrogen explosions before the burning, welding, or repairing of hydrogen chloride equipment, there must be an explosion test to verify safe conditions.

All metal equipment must be dried with nitrogen or dry air to below a -40 C dew point before anhydrous hydrogen chloride is introduced.

Acid-resistant paint should be used on buildings, equipment, and piping in the vicinity of anhydrous hydrogen chloride equipment, and regular external inspections should be conducted to identify and correct areas of external corrosion. Piping and vessels used in pressure service are hydrostatically tested on a regular schedule, to ensure the integrity of the equipment.

Overpressure Relief and Emergency Vents

Anhydrous hydrogen chloride equipment is protected against overpressure by rupture disks or relief valves at code-specified ratings. Where rupture disks are used, impervious graphite or silver disks are specified. Relief valves are generally of the spring-loaded type as used on chlorine tank cars, but with silver lower frangible disks (lead lower disks are used for chlorine relief valves). The frangible disk shields the working parts of the relief valve from hydrogen chloride until relief pressure is approached.

The discharge of pressure relief devices should be directed to an absorber to prevent atmospheric release of hydrogen chloride. Emergency vents to the absorber are provided at stratetic points in the process, to prevent atmospheric emissions due to equipment shutdown, power outage, or reaction control problems.

Additional precautions must be taken in the handling of anhydrous hydrogen chloride liquid. Expansion vessels should be provided for piping systems where the liquid could be blocked between closed valves. Thermal expansion and increased vapor pressure due to a temperature increase can create a hazardous overpressure without expansion vessels. For the same reason, the design must include a way to prevent overfilling of an anhydrous hydrogen chloride liquid container or vessel.

Tail-Gas Absorption and Emergency Emission Control

Elimination of tail-gas streams of anhydrous hydrogen chloride and emergency emission control are accomplished through absorption of the gas in a water jet, fume scrubber, or packed tower that circulates water or a dilute alkaline solution. Absorber design must provide for the removal of heat generated by the absorption process. A barometric loop on the tail-gas stream must prevent suckback of the absorption liquid into the process.

Response to a hydrogen chloride leak must be as quick as possible, because the leak will increase in severity. The leaking hydrogen chloride will combine with atmospheric moisture and form corrosive hydrochloric acid at the point of leakage. The acid will further attack the steel pipe or container and increase the leak. Proper respiratory protection and, in many cases, protective clothing should be put on before the leak is approached. A dilute aqueous ammonia solution or a cloth saturated with ammonia is used to find the leak. Where the ammonia vapor contacts hydrogen chloride, a white "smoke" (ammonium chloride) will be formed. When the leak is found, the defective piping or equipment must be isolated, purged of hydrogen chloride with dry air or nitrogen, and repaired or replaced.

In the event of a large emission to the atmosphere, a fog nozzle spraying large quantities of water should be used to absorb the hydrogen chloride until its source can be shut down. Unlike chlorine, hydrogen chloride is very soluble in water, and fog nozzles are effective in controlling emission. Care should be taken to direct the water away from the point of leakage to avoid increasing the leakage by aggravated corrosion.

Protection of plant personnel and other persons in the area affected by a hydrogen chloride release must be the prime concern in the response to a release. Emergency planning, personnel training, and coordination with local authorities should be handled as discussed earlier in this chapter.

ANHYDROUS HYDROGEN CHLORIDE TRANSPORTATION

Anhydrous hydrogen chloride is transported as a pressurized liquid in cylinders of 50 and 600 lb (22.5 and 270 kg) net, truck tube and tank trailers, and tank cars. The pressure in anhydrous hydrogen chloride containers depends on the temperature of the liquid. At 68 F (20 C), the pressure is about 600 psig; it is less at lower temperatures. Gaseous or liquid hydrogen chloride may be withdrawn from cylinders, but the larger containers are designed only for liquid withdrawal. All containers used in the transportation of anhydrous hydrogen chloride are controlled by federal or other governmental regulations, and it is the responsibility of each person shipping, transporting, or using anhydrous hydrogen chloride to know and comply with all applicable regulations. The design of the containers commonly used is discussed briefly below.

Containers

Anhydrous hydrogen chloride cylinders are steel pressure vessels constructed in accordance with DOT specifications. The 22.5-kg cylinders are equipped with a top discharge valve and two safety devices designed to relieve at pressures of 2,400-2,700 psig and temperatures of 158-163 F (70-73 C). One relief device is on the valve body, and the other is in the concave cylinder bottom. Gaseous hydrogen chloride is withdrawn from the 22.5-kg cylinder in an upright position, and the cylinder may be inverted to withdraw liquid. The 270-kg cylinders are handled on their sides and are equipped with one discharge valve and three relief devices. Two of the relief devices are on the cylinder proper, and one is on the discharge valve. They are rated at pressures of 2,400-2,700 psig and temperatures of 70-73 C. The discharge valve is connected to an internal dip tube that permits withdrawal of either liquid or gaseous hydrogen chloride by rotation of the cylinder. Cylinder valves are protected by a valve hood, which should be in place at all times when the cylinder is not in use. Normal cylinder handling precautions must be taken for safe operation. The cylinders must be secured when stored, protected from dropping or striking, stored in a cool dry place, and protected from sunlight or other heat sources.

Anhydrous hydrogen chloride tube trailers are made in various sizes and are basically multicylinders mounted on a trailer and manifolded together. Common tube trailers transport 5-8 tons (4,500-7,200 kg) of anhydrous hydrogen chloride, although other sizes are also used. Each individual tube or cylinder on a tube trailer has a block valve and relief devices designed to relieve at pressures of 2,400-2,700 psig or temperatures of 70-73 C. Manifold designs, tube design, and configuration vary within the DOT specifications. Manifold arrangements on tube trailers are designed only for liquid hydrogen chloride withdrawal. In tube trailer processing and refilling, care must be taken to prevent overfilling an individual tube. A vacuum is pulled on each tube, the vacuum broken with dry air, the tube valve removed, and the tube visually inspected for foreign matter. If foreign material is present, the tube must be cleaned before loading. All tubes must be dried to below a -40 C dew point. Each tube is individually loaded by weight to a filling density of not over 65% (percent ratio of the weight of hydrogen chloride in the container to the weight of water that the container will hold). A few single-bore tank trailers in anhydrous hydrogen chloride service are in operation under a special permit.

Rail tank cars of various sizes are in use to transport anhydrous hydrogen chloride, with the most common having capacities of 33 and 70 tons (29,700 and 63,000 kg). The cars are designed for liquid hydrogen chloride withdrawal and are equipped with relief valves like those on chlorine cars. The lower frangible disk in the relief valve is silver, rather than lead, as is used in chlorine cars. A special DOT permit is required for selected hydrogen chloride tank cars for specific routing to transport anhydrous hydrogen chloride liquid. The relief-valve setting for most hydrogen chloride tank cars is 450 psig, which is below the vapor pressure of liquid hydrogen chloride at normal ambient temperatures. The hydrogen chloride is refrigerated to -50 F (-45.6 C) before loading into the insulated tank car. This allows 30 days or more before the liquid temperature will approach the corresponding vapor pressure to lift the spring-loaded safety valve. The monitoring and expediting of hydrogen chloride rail shipments and the complete withdrawal of all liquid hydrogen chloride by the consumer receiving the tank cars are necessary, to prevent hydrogen chloride release. The standard emergency kit used for chlorine cars will fit most anhydrous hydrogen chloride cars to control leaks, but its use must be accompanied by additional action to lower the tank-car pressure, because the chlorine emergency kit is designed for lower pressures than are commonly experienced with hydrogen chloride.

Two properties of anhydrous hydrogen chloride can be useful in responding to in-transit leaks:

- Through withdrawal of gaseous hydrogen chloride from a container, vaporization of the liquid removes about 190 BTU/lb vaporized. This reduces the temperature of the remaining liquid and reduces the pressure in the container.
- Unlike chlorine, hydrogen chloride is readily soluble in water. In a situation where the container pressure must be lowered, gaseous hydrogen chloride can be withdrawn and absorbed by water. Use of a fog nozzle to spray water on an emission is effective in controlling the emission.

General guidelines for responding to a hydrogen chloride leak are similar to those discussed for chlorine. The major differences are the higher pressures used in transporting hydrogen chloride, the favorable water solubility of hydrogen chloride, and the availability of the emergency devices for all chlorine containers.

Pipelines

Gaseous anhydrous hydrogen chloride is transported via steel pipelines for interplant transfer and delivery to nearby customers. Design, maintenance, and safe operation of these pipelines involve the factors discussed earlier in connection with the materials of construction and corrosion control. The design must permit adequate purging, washing, and hydrostatic testing. The line must be protected from being struck by traffic or heavy equipment, and below-grade lines must be encased at grade crossings. Underground pipe should be cathodically protected from external corrosion. The pipelines should be all-welded steel, with expansion loops where required.

Inspection of the external condition of the pipeline and periodic hydrostatic testing of the line are important for safe operation.

Emergency procedures for a hydrogen chloride pipeline leak primarily involve shutting off of the gaseous feed to the pipeline and dumping of the line pressure to the emergency vent absorber. Protection of people in the affected area and "fogging" of the emitted hydrogen chloride gas with water to minimize the atmospheric release are integral parts of the emergency plan for a specific installation.

INDUSTRIAL HYGIENE

Recommended industrial hygiene practices for a chlorine or anhydrous hydrogen chloride area in a plant are as follows.

Medical Aspects

A new employee or one about to be reassigned to a chlorine or hydrogen chloride area should receive a physical examination, and his medical history should be reviewed. The physical should be a thorough, general examination, with emphasis on discovering evidence of chronic respiratory, pulmonary, or cardiac difficulties. A person with such chronic difficulty should not be assigned to a chlorine or hydrogen chloride handling area.

Routine medical surveillance involves regularly scheduled reexamination of employees and review of recent illness history.

Plant Design, Operation, and Maintenance

The engineering design of an area in which chlorine or hydrogen chloride is to be handled must include proper ventilation, to avoid gas accumulation in case of leakage. There should be provisions for handling a process upset without exposing employees to an atmospheric release. Alarms, emergency vent systems, absorption systems, etc., should be installed where appropriate. High housekeeping standards should be maintained. A formal emergency plan for handling an atmospheric release should be devised, and employees should be trained in its application. Retraining and regular drills for specific emergencies or release situations are important.

Equipment and controls should be tested often to ensure proper operation when needed. Leaks should be promptly repaired.

Respiratory Protection

Employees should be trained in the location and use of canister gas masks and self-contained breathing apparatus. It is recommended that every employee entering a chlorine or hydrogen chloride area be provided with a pocket escape respirator and carry it at all times. The proper use, location, and maintenance of the various respiratory protection devices should be reviewed regularly.

Periodic air sampling and determination of the weighted exposure of each employee group is recommended for information and control purposes.

Both chlorine and hydrogen chloride leaks can be easily found with ammonia, and the characteristic odor of each below the recommended TLV can be detected. Prompt identification and correction of leaks are the main criteria of an effective industrial hygiene program in a plant that produces or consumes chlorine or hydrogen chloride.

CHAPTER 9

SUMMARY AND CONCLUSIONS

ATMOSPHERIC SOURCES AND TECHNIQUES OF EMISSION CONTROL

Volcanic gases constitute the only known natural source of emission of chlorine and hydrogen chloride gases to the atmosphere, and the quantities of such emission are minute. The formation of chlorine in low concentrations by atmospheric reactions has been postulated. Atmospheric reactions leading to the formation of hydrogen chloride gas in low concentrations have also been postulated.

Commercial production of chlorine is a major and growing U.S. industry. A total of 9.86 x 10^6 tons (8.9 x 10^9 kg) of chlorine was produced in the United States in 1972, and production is projected to continue to increase at approximately 7% per year through 1974. Chlorine gas and liquid shipments in 1971 total about 4.2 x 10^6 tons (3.8 x 10^9 kg), or 45.4% of the total production of 9.35 x 10^6 tons (8.4 x 10^9 kg) in 1971.

The production, shipment, and use of chlorine provide significant opportunities for infrequent, localized emission of chlorine to the atmosphere, through equipment or control system failure or transportation accidents. Improved engineering design (including the use of fail-safe systems), improved selection of materials of construction, and appropriate detailed local and national emergency plans are being used to minimize the incidence and magnitude of such accidental releases of chlorine to the atmosphere and to minimize their effects on the public. No estimate can be made of the chlorine emission to the atmosphere from such accidental and noncontinuous emissions.

Potential continuous emission of chlorine from production and use is controlled by the recycling of exit gases to plant chlorination processes, the neutralization of chlorine in alkaline scrubbing units, and the scrubbing of chlorine from gas streams with a solvent and then recovery of the chlorine from the solvent. Scrubbing technology is well developed, and the industrial use of such technology is extensively reported in the literature. The use of a final alkaline scrubber on the process tail-gas emission to the atmosphere is common industrial practice, regardless of the type of intermediate chlorine emission control technique.

The chlorine emission factor for any production or use is a direct function of the type of final emission control technique used to treat the process tail gases. The chlorine emission factor can be reduced to a few parts per million (pounds of chlorine emitted per million pounds of chlorine handled or product produced) through the use of final alkaline scrubbing, but the absence of final alkaline scrubbing will permit chlorine emission factors ranging up to values like 10-20 lb of chlorine emitted per ton of chlorine handled or product produced, depending on the process and the chlorine emission control techniques (if any) used. Processes with chlorine emission factors in the range of 10-20 generally have no emission control system on the purge stream. A chlorine emission factor of less than 1 is normally obtained when a nonalkaline chlorine emission control system is used.

In view of the nonuniformity in the techniques used to control potential chlorine emission to the atmosphere, no attempt has been made to estimate the maximal annual emission of chlorine to the atmosphere from continuous sources.

Commercial production of hydrochloric acid (100% basis) in the U.S. in 1972 was 2.2 x 10^6 tons (2 x 10^9 kg), and production is projected to increase over the next few years at an average annual rate of approximately 5-7%. In 1972, 90% of the hydrochloric acid (100% basis) was manufactured as a byproduct of the chlorination of organic compounds. Theoretically, practically all the hydrochloric acid produced by the three major routes is available for release to the atmosphere as hydrogen chloride gas; in practice, the potential emission is most commonly, effectively, and inexpensively controlled by scrubbing the main exit-gas stream and any tail-gas stream with water. Other emission control systems have been developed to meet special industrial requirements.

The published data indicate that adequate technology and control equipment are available to reduce hydrogen chloride emission from byproduct process manufacturing and from applications of hydrogen chloride gas to about 0.5 lb/ton (0.25 kg/1,000 kg) of 20° Bé acid produced. In such cases as the manufacture of hydrogen chloride by the synthesis process, or where hydrogen chloride is the only component to be removed from a tail-gas stream, water scrubbing can reduce hydrogen chloride emission to less than 0.1 lb/ton (0.5 kg/1,000 kg) of 20° Bé acid produced.

If we assume that almost all continuous emission of hydrogen chloride gas from primary manufacturing and applications is water-scrubbed to prevent local public-nuisance and plant-corrosion problems and if we assume a hydrogen chloride emission factor of 0.5 lb/ton (0.25 kg/1,000 kg) of 20° Bé (31.5% hydrogen chloride) acid produced, then approximately 1,750 tons (1.6 x 10^6 kg) of hydrogen chloride gas was emitted to the atmosphere in the United States in 1972 from such manufacturing and applications. This rough estimate also assumes the use of low concentration aqueous acid (less than 20%, with negligible hydrogen chloride equilibrium vapor pressure) for the bulk of the applications.

It should be noted that the byproduct hydrogen chloride is believed to be considerably in excess of what is recovered and reported and that the disposition of such excess is unknown. Consequently, these estimates of hydrogen chloride gas emission to the atmosphere from byproduct process operations are undoubtedly low, but no reliable basis is available for the development of a more accurate estimate.

As is the case with chlorine, the production and use of hydrochloric acid (100% basis) provide significant opportunities for infrequent, localized emission of hydrogen chloride gas to the atmosphere, through equipment or control system failure. Transportation accidents with hydrochloric acid (100% basis) are significantly less serious than chlorine transportation accidents, because most hydrogen chloride is shipped as 18°, 20°, and 22° Bé* aqueous hydrochloric acid solutions and because the great affinity of the gas for water permits reasonable control of large emission through use of fog nozzles. Improved engineering design (including fail-safe systems), improved selection of materials of construction, and appropriate detailed emergency plans are being used to minimize and control accidental releases of hydrogen chloride gas to the atmosphere.

On the basis of limited data, the public incineration of approximately 30×10^6 tons (27×10^9 kg) of collected refuse in the United States in 1970 produced an estimated maximal atmospheric emission of 75,000 tons (67.5×10^6 kg) of hydrogen chloride gas. The hydrogen chloride emission arises from the combustion of chlorine-containing plastics, especially polyvinylchloride, in the refuse and from the combustion of other components of the refuse that contain chlorine or chlorides, probably largely in the form of common salt (sodium chloride). No free chlorine or phosgene has been detected in the exit gases from refuse incineration. Only in the last few years have true wet-scrubbing systems, as differentiated from crude spray chambers or wet baffles, been applied to municipal incinerators to afford favorable conditions for removing such gases as sulfur dioxide, hydrogen chloride, and organic acids from the flue-gas streams. At present, fewer than 10% of incinerators have wet-scrubbing systems. The projected increases in public incinerator capacity to 58 x 10^6 tons (52 x 10^9 kg) and in the plastics component of refuse from the present 2% to 2.8-3.0% by 1980 will significantly increase the potential for hydrogen chloride emission to the atmosphere, even if the present percentage distribution of polyolefins, polystyrene, and polyvinylchloride in the plastics component of refuse remains unchanged.

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*18°, 20°, 22° Bé is 27.9%, 31.5%, and 35.2% acid, respectively.

The combustion of fossil fuels, particularly coal, produces a major contribution to the chloride content of the atmosphere in the form of hydrogen chloride gas emission. The United States consumed about 526 x 10^6 tons (474 x 10^9 kg) in 1970. If it is assumed (using published data) that the average chlorine content of coal is 0.128% and that 95% of the chlorine is converted to hydrogen chloride gas, it is possible to estimate the maximal hydrogen chloride gas atmospheric emission due to coal burning in 1970 at 0.64 x 10^6 tons (0.6 x 10^9 kg) although methods are available for control of emission of sulfur dioxide, nitrogen oxides, and hydrogen chloride from coal- and oil-fired industrial heating plants and electric generating plants, these methods are not in general use.

There appears to be little published information on the measurement of gaseous chlorine or hydrogen chloride in exhaust from any mode of transportation. In fact, there is no evidence that there is such gaseous emission.

Although appropriate exhaust analysis data do not exist, one can calculate that the maximal theoretical amount of hydrogen chloride gas (the contaminant assumed to be emitted) that could be emitted from mobile sources burning motor gasoline in the United States in 1971 is approximately 26,000 tons (23.4×10^6 kg). It seems reasonable to assume that other chlorides--such as lead chloride, ammonium chloride, and hydrocarbon chlorides--may be formed, so even this maximal theoretical emission of hydrogen chloride gas is probably high. In any case, such postulated hydrogen chloride emission from mobile sources will decrease significantly in future years, as the lead content of gasolines is decreased.

The contribution of NASA launch vehicles to environmental pollution due to emission of hydrogen chloride gas appears to be much smaller than those of other sources of such pollution. Hydrogen chloride emission from the Titan vehicles represents the only environmental hazards of significance contributed by NASA OSS Launch Vehicle and Propulsion Programs, and NASA concludes that this hazard is modest and that, even under unfavorable meteorologic conditions, it is estimated to be confined to controlled areas. The NASA conclusion is based on an assessment of the environmental effects of operations involving the current and near-future launch vehicles that will be used up to about 1979-1980. The Space Shuttle, which is intended to replace most of the current family of launch vehicles and is expected to be operational about 1979-1980, will emit only water vapor and free hydrogen from the combustion process.

ATMOSPHERIC CHEMISTRY

There is very little information on the concentrations of gaseous chlorine compounds in the nonurban atmosphere. There is no direct evidence of their chemical form, but it is generally believed to be hydrogen chloride.

In marine air, the gaseous chlorine concentration near sea level is about 3 μg/SCM, where particulate chlorine (in sea salt) generally ranges from 1 to 10 μg/SCM. The source of the gaseous chlorine in marine air is not definitely known, but it is probably atmospheric sea salt particles. Volcanism may be a less important source. Experimental evidence suggests that the residence time of gaseous chlorine is longer than that of the chlorine present on particles.

There is very little information on the nature and concentration of chloride in urban air of American cities. On the basis of a few limited data, it appears that the concentrations of total chloride exceed those in nonurban and marine air by a factor of about 10 and that they are in the range of 10-100 $\mu g/m^3$, away from sources. The principal chloride-containing gas in urban air is expected to be hydrogen chloride. Data on particulate chloride in cities are also scarce, but the available information suggests that such concentrations are similar to those in the uncontaminated marine atmosphere--less than 5 $\mu g/m^3$. Halogen-carrying pesticides contribute little to the chloride burden, although they are known to decompose in the atmosphere.

Chlorine compounds can undergo a variety of photochemical reactions in the atmosphere that may be potentially significant in ozone formation and removal. Hydrogen chloride can be released from particulate chloride by reactions of acid gases, such as nitrogen dioxide, in the presence of moisture.

At the concentrations currently known, there is no evidence that chlorine compounds play any significant role in the chemistry of polluted atmospheres or in inadvertent weather modification.

With the exception of pesticides, chlorine-containing compounds are expected to be removed rapidly from the atmosphere. Their residence time in urban air should be similar to that in nonurban air. Rough calculation indicates a gaseous chloride atmospheric residence time of 2-17 days.

The most crucial problem at present in dealing with the urban chemistry of airborne chlorine is the lack of data on ambient concentrations of gaseous and aerosol chlorides.

EFFECTS ON MAN AND ANIMALS

Chlorine

Excessive exposures to chlorine have proved fatal to both man and microbe. But, as Paracelsus said in the early 1500's, *dosis sola facit venenum* ("the dose alone makes a poison"). This is true for chlorine. One of the earliest applications of chlorine was as a war gas. However, observations made on front-line troops exposed to it during World War I led to its later use, at reduced concentrations, as a treatment for respiratory tract infections.

Although chlorine gas has a wide variety of current uses, none of them results in the intentional exposure of mammals, including man. Because the material is ubiquitous, however, acute and chronic inadvertent exposures do occur.

A wide variety of effects are reportedly associated with exposure to chlorine gas, but those involving the respiratory system are considered the most significant. Chlorine has intermediate solubility in water and therefore produces its irritant effects on both the upper and lower passages of the respiratory system. The physiologic response to exposures varies from odor perception to pulmonary edema and death. This response is influenced not only by concentration and duration of exposure, but also by species and even individual variability.

Odor threshold has been reported as low as 0.02 ppm and as high as 3.5 ppm. Minimal mucous-membrane irritation shows similar variability: 0.2-16 ppm. Part of this wide range can be attributed to biologic variability, variation in individual tolerance and differences in test techniques or methods of evaluation. One researcher may use the lowest concentration to elicit a response in the most sensitive subject as the threshold; another may use the concentration that produces the same response from all members of a panel of experts as the threshold.

A single chlorine gas exposure can produce signs of acute obstructive airway disease that usually resolves with symptomatic treatment by qualified physicians. Whether it resolves completely, whether intermittent significant exposures cause permanent pulmonary changes, and whether chronic low-concentration exposures result in pulmonary disease are still being debated. Some researchers, on the basis of postexposure pulmonary-function studies, believe that permanent pulmonary changes can occur as a result of single or intermittent severe exposures. Others, analyzing the same data, disagree. It should be noted that these are retrospective studies and that no baseline pulmonary studies were available; therefore, "significant changes" had to be inferred from "population norm." There is another problem in analyzing for the significance of chlorine gas exposures: cigarette-smoking. For the most part, the significance of cigarette-smoking in the pathogenesis of pulmonary disease in victims of chlorine gas exposure has been ignored. Morbidity studies of personnel gassed in World War I, for example, seem to presume that all lung abnormalities were a result of the gassing and completely disregarded other etiologies for lung pathology. Where cigarette-smoking has been considered, evidence indicates that it is at least as significant as chlorine exposure in the development of abnormalities of pulmonary function.

Studies of workers chronically exposed in the work environment to low concentrations of chlorine gas (time-weighted averages of 0.006-1.42 ppm, with a mean of 0.146 ± 0.287 ppm) show no significant pulmonary changes, in comparison with a control population matched for age, smoking history, etc.

This is not to say that similar low-concentration exposures would be safe for the general population. The industrial population is relatively healthy and exposed to the material in an oscillating fashion (8 hr "on," 16 hr "off," 5 days out of 7). The general population potentially could be continuously exposed to low concentrations. Also, it contains various subgroups that might be more susceptible to the adverse effects of chlorine. These subgroups may include the young, the old, and those with acute and chronic respiratory problems, such as pneumonia, asthma, and emphysema. Additional populations at risk may be those with cardiovascular problems, heavy smokers, people with an $\alpha \underline{1}$ antitrypsin deficiency state, and even healthy people after heavy exercise.

Hydrogen Chloride

Because of the chemical characteristics of hydrogen chloride, significant biologic effects are limited to the teeth, the respiratory tract, and, to a lesser extent, the integument. These very characteristics, however, provide hydrogen chloride with good warning properties and thus protect most people from the harmful effects of acute exposures. Although laryngeal spasm, pulmonary edema, and death can occur from exposures to gaseous hydrogen chloride, the effect is usually only a mild, transitory upper respiratory tract irritation. If able to do so, most people remove themselves voluntarily from concentrations that are potentially hazardous.

Minimal response has been noted at concentrations as low as 0.067 ppm, and no response at concentrations as high as 35 ppm; however, most authors agree that exposures become disagreeable at 5-10 ppm. People who are chronically exposed apparently can develop a tolerance to the material and exhibit none of the symptoms of irritation or changes in pulmonary function that are found in those acutely exposed to similar concentrations. The only effect of chronic exposure to low concentrations of gaseous hydrogen chloride appears to be erosion of the incisors.

Although gaseous hydrogen chloride has not been reported to possess any mutagenic, teratogenic, or carcinogenic potential, it has been recently noted that high concentrations of hydrogen chloride and formaldehyde can react under atmospheric conditions to form bis-chloromethylether, a material of reported malignant potential.

As for groups potentially at increased risk, most of the published data deal with acute, subacute, or chronic exposures of laboratory animals or industrial workers--both relatively healthy subgroups of their populations. The effects of exposure to gaseous hydrogen chloride on the young, the old, and the infirm have not been explored; these may be the groups at highest risk. Ruminants, in light of the data on dental erosion, may also be at increased risk of morbidity.

EFFECTS ON PLANTS

Chlorine

There is a surprising amount of information available on chlorine pollution in the air, despite the fact that it does not appear to be a widespread or economically significant air pollutant. The reports of field damage indicate that injury from this pollutant is rather infrequent, and that, when it does occur, it is usually as a result of an accident or negligence.

Our knowledge of the comparative toxicity of chlorine gas to members of the plant kingdom encompasses bacteria and fungi, as well as higher plants, but that knowledge appears to be very shallow. There is little or no information on several types of plants--for example, fruit and nut crops, field and forage crops, and forest trees.

Leaves of higher plants are more sensitive to chlorine than fungi, bacteria, stems, seeds, and sclerotia. The symptoms most often observed on higher (broadleaf) plants are interveinal necrosis (usually close to the margin and progressing toward the midrib), white to tan markings, and an overall bleaching of leaves. The characteristic response on conifers is an orange to reddish-brown discoloration at the tip of the needles at high concentrations, and bleaching at low concentrations.

The sensitivity of plant species is modified by age, soil moisture, water stress, and dormancy.

Chlorides accumulate in plant tissues after fumigation, but the accumulation does not appear to be related to exposure concentration or to the amount of tissue damage.

There seems to be a serious gap in our knowledge of chronic and metabolic effects. Reported episodes of plant damage from chlorine gas have been accidental and have usually produced acute effects, and it is not surprising that what research has been done on chlorine gas has reflected the nature of the problem. However, information on chronic and metabolic effects should be obtained before considering establishment of standards. Because chlorine is involved in photosynthesis, it is important to determine what chronic exposure to chlorine would do to yields of various crops.

Hydrogen Chloride

The lack of detailed information on the effects of hydrogen chloride gas on plants is probably a reflection of its unimportance as a generally distributed phytotoxicant. Because this gas can be easily scrubbed from flue gases and because its major sources are point sources, there has not been any urgency to mobilize research efforts in the descriptive pathologic effects of this contaminant. It is obvious from the minuscule amount of research that has been done, however, that the gas can have serious effects on plant life at very low concentrations. Because of the increased use of halogen-bearing plastics in modern society and the disposal of such plastics by incineration, hydrogen chloride gas may become a more common air contaminant. In view of the limited available information, one can only conclude that the data base for the establishment of an air quality standard for this gas is extremely narrow.

Unfortunately, many of the conclusions derived from early experimental work are no longer tenable, particularly those dealing with dose response, because of improper fumigation methods. The field observations, however, are presumably still valid, although early researchers seemed to be more concerned about damage by hydrochloric acid than that by hydrogen chloride gas.

One should be cautious in extrapolating results obtained under rigidly controlled laboratory conditions to outdoor situations, because of the problems associated with monitoring for hydrogen chloride and because of the atmospheric reactions of hydrogen chloride. Plants respond differently to a gas and to an acid aerosol, so the determination of the form of the chloride reaching the plant is as important as the degree of exposure. Future research with these two gases should reflect the expected range of atmospheric conditions.

Recent investigations indicate that chronic effects can be expected at 0.40 ppm, and acute effects at a few parts per million (≈ 1-20 ppm), depending on the species. Perhaps the most significant conclusion to be drawn from recent work is that relative humidity appears to be the governing factor in plant response. As opposed to the plant response to sulfur dioxide in relation to relative humidity, which is essentially linear, there appears to be a threshold of relative humidity above which plants will incur twice as much damage at a given dose. This phenomenon may be related to the hygroscopicity of the gas, the mode of entry, and later injury caused by the gas phase, as opposed to the acid phase. The point is very important to resolve, because it has such a crucial bearing on the establishment of a standard for this gas.

Hydrogen chloride gas causes glazing on the lower surface of the leaf similar to peroxyacetyl nitrate injury, and microscopic symptoms resemble those caused by hydrogen fluoride, sulfur dioxide, and smog. Only limited information is available on the relative sensitivity of various plant species.

The physiology of uptake, distribution, and accumulation and the effects of hydrogen chloride is still poorly known, although it has been studied to a limited extent. It appears that, at least in the gas phase, hydrogen chloride enters through stomata and accumulates as chlorides in the foliar parts of the plant. It is not known whether the injury is due to the acidity of the gas, to the toxicity of the chloride, or both.

PROPERTY DAMAGE AND PUBLIC NUISANCE

The lack of data on atmospheric concentrations of chlorine and hydrogen chloride or the acceleration of atmospheric corrosion caused by them prevents firm conclusions at this point. All that can be said is that hydrogen chloride and chlorine in the atmosphere at some concentration will cause acceleration of atmospheric corrosion. Whenever there is a major release of chlorine or hydrogen chloride, there will be a major increase in atmospheric corrosion, which will depend heavily on meteorologic conditions, such as humidity, temperature, and wind velocity. It is not known how chlorine or hydrogen chloride in combination with other pollutants would act.

Obnoxious odors are poorly defined. There is some disagreement with respect to the olfactory threshold concentrations of chlorine and hydrogen chloride.

Trace amounts of chlorinated organics produced in minute quantities at chlorine plants are often identified as chlorine by the general public when referring to the characteristic odor of a chlorine plant.

Unquestionably, the threshold concentrations presented in this report will cause human discomfort. However, they will occur only when there are substantial releases of chlorine or hydrogen chlorine. Derivatives of chlorine that are coincidentally produced in trace amounts on the premises of chlorine plants are highly unlikely to cause any discomfort to the general public.

SAFETY IN USE AND HANDLING

Safe handling and emission control are on a solid base in the manufacture and use of chlorine and anhydrous hydrogen chloride. Engineering, operating, and maintenance safeguards are well established for these materials.

Exclusion of moisture from chlorine and anhydrous hydrogen chloride equipment is the most important element in controlling corrosion.

The high solubility of anhydrous hydrogen chloride in water provides an effective method for controlling hydrogen chloride emission. Water cannot be used in controlling chlorine emission.

The chlorine industry has developed standardized containers, emergency devices for stopping container leaks, and emergency teams for response to chlorine leaks. These have been highly beneficial in controlling and correcting leaks.

The construction and use of anhydrous hydrogen chloride containers are regulated by the Department of Transportation. They are not standardized.

The major factors in the proper response to a chlorine or hydrogen chloride leak are prior establishment of an emergency plan, trained personnel, access to respiratory protective equipment, access to emergency devices for stopping container leaks, coordination with local authorities, and first-aid facilities and trained first-aid personnel.

The response will vary with the type of leak, the equipment, the location, etc., but the emergency plan should include provisions for stopping the leak, minimizing the gas emission, and protecting persons in the affected area.

CHAPTER 10

RECOMMENDATIONS

ATMOSPHERIC CONCENTRATIONS AND EMISSION CONTROL TECHNIQUES

Surveys should be conducted by the EPA or other governmental agencies or nongovernmental associations or organizations, to determine the concentration of gaseous and particulate chlorine compounds in the atmosphere in selected urban and nonurban areas and their sources. Survey results from areas that have a heavy concentration of chlorine-producing or -using plants should be compared with survey results from industrial areas that have few potential chlorine emission sources; this would contribute to an understanding of the magnitude of an atmospheric chlorine concentration problem and thereby assist in the development of whatever chlorine emission guidelines or standards are deemed necessary.

Emission gas that contains chlorine should be alkaline-scrubbed before being emitted to the atmosphere.

All cell-room chlorine header seals in electrolytic process plants that manufacture chlorine should be piped to a lime or caustic scrubber for absorption of cell chlorine when seals blow owing to backpressure.

If hydrochloric acid is air-blown to remove traces of organics, this should be done in a vessel equipped with a water scrubber or ejector for emission control.

New or modernized public incinerators in the United States should be equipped with wet-scrubbing systems for control of emission of particles, sulfur dioxide, hydrogen chloride, and organic acids.

No attempt was made to estimate the maximal potential hydrogen chloride emission from the combustion of fuel oils, because little information was available on the average chlorine content of fuel oils. Inasmuch as fuel oil amounted to 16% of the total fuel used in 1970, the chlorine content of fuel oils should be determined.

Further research and development work is needed in the design and selection of materials of construction for public incinerator internal components, to minimize corrosion problems and to ensure the proper feeding and complete combustion of refuse.

Continued research and development work is urgently needed on commercially useful systems for control of emission of sulfur dioxide, nitrogen oxides, and hydrogen chloride from large stationary fossil-fuel (particularly coal) industrial heating plants and electric generating plants.

ATMOSPHERIC CHEMISTRY

The chemical forms of gaseous chlorine in nonurban and urban air should be determined.

The major reactions of gaseous chlorine compounds with other atmospheric constituents should be studied, with particular attention to photochemical interactions.

The major sinks and the mean residence time for atmospheric gaseous and particulate chlorine should be determined, with special emphasis in cities on building surfaces and vegetation.

EFFECTS ON MAN

Chlorine

Physicians experienced in the handling of cases of chlorine inhalation, under the auspices of the Chlorine Institute, have put together a set of recommendations for the medical evaluation of patients suffering from chlorine exposures. Their recommendations should be distributed to and followed by all physicians likely to treat patients exposed to chlorine.

Prospective studies of the effects of chronic exposure to low concentrations of chlorine should be conducted, so that the debate as to the significance of such exposure can be concluded.

Hydrogen Chloride

Further studies should be conducted on population subgroups potentially at increased risk. The problem of the spontaneous reaction of gaseous hydrogen chloride with other atmospheric contaminants to produce carcinogens should be evaluated in detail.

EFFECTS ON VEGETATION

Chlorine

Studies should be undertaken to determine the injury threshold concentrations of chlorine gas. Such studies should be done on a wide variety of plants representing several classes.

Diagnostic methods should be developed to aid in field identification of air pollution damage. If a suitable chemical method for tissue analysis cannot be developed to determine positively whether damage was caused by chlorine gas, then it will be necessary to determine the entire spectrum of response, and symptom expression will have to be studied in detail.

Hydrogen Chloride

There is need to expand knowledge further on the sensitivity of plant species to hydrogen chloride gas. A number of species representing different classes of plants should be tested to determine the exposure to the gas that can be tolerated without injury. There is a need to standardize fumigation methods, to fill gaps in the knowledge of plant response and to permit comparison of results from various researchers.

Additional information is needed on synergistic effects of hydrogen chloride with other common air pollutants on a number of plant species. Nothing is known of the effects of this gas on yield impairment, flowering, and community or ecologic effects. And nothing is known of the effects on soil and soil microbes or of the fate of the chloride once it enters the food chain.

Diagnostic methods for field evaluation of symptoms are needed. Because the symptoms caused by hydrogen chloride can be easily mistaken for those caused by other agents, reliable sampling techniques and laboratory procedures need to be developed.

PROPERTY DAMAGE AND PUBLIC NUISANCE

The concentrations of chlorine and hydrogen chloride should be determined at the perimeter of property that contains emitting sources or potential emitting sources, such as plants that produce or use chlorine or hydrogen chloride (paper mills, chlorinated organics plants, water treatment plants, etc.). Similar measurements should be made at coal-burning power plants and incinerators. Such a program would determine whether a pollution problem exists and, if so, define its extent.

Because there is some indication that chlorine and hydrogen chloride contribute to atmospheric corrosion, it is important to determine whether the contribution is significant. This can be done by establishing a program in which specimens of various materials--such as painted and unpainted metals, fabrics, and limestone--are placed where chlorine or hydrogen chloride is known to be present in the atmosphere. In such a program, analyses should be carried out to determine the concentration of sulfur oxides, nitrogen oxides, and other species that are known or suspected to contribute to accelerated atmospheric corrosion. Meteorologic conditions--

such as hours of sunlight, humidity, temperature, and wind velocity and direction--should also be closely monitored. Besides providing insight into the influence of hydrogen chloride and chlorine on accelerated atmospheric corrosion, it would yield information on the influence of other chemical species on atmospheric corrosion and their interactions. Test specimens would then be examined to determine corrosion products, as well as changes in appearance, physical properties, and weight.

Additional research is required to determine what constitutes an obnoxious odor. It is also necessary to develop an unambiguous, quantitative method of determining odors. The extent to which chlorine and hydrogen chloride interact with other odorous species, which might be present in the atmosphere, to produce an increased odor must also be established.

The development of a method for identifying the trace quantities of chlorinated organics that impart the characteristic odor to chlorine plants might be considered, as well as techniques to control their release.

SAFETY

Producers and repackagers of chlorine and anhydrous hydrogen chloride should continue to conduct safety seminars and film and slide presentations and to supply technical bulletins, etc., to users, transporters, and others involved in handling these materials.

Training geared to responding to emergency situations involving chlorine and hydrogen chloride containers should be made available to local emergency teams, firemen, etc. Although not directly involved with chlorine handling, these groups will get the first call in some leak situations and should be trained in the proper response.

The need for container standardization and emergency devices for container leaks should be evaluated for anhydrous hydrogen chloride transportation. The past record, the use of water with hydrogen chloride for emission control, etc., should be considered.

Chlorine and anhydrous hydrogen chloride producers should continue to strive to use fail-safe systems in the manufacturing plants.

ANALYTIC TECHNIQUES

Several titrimetric and colorimetric methods are commonly used for the determination of elemental (available) chlorine. These have been evaluated by individual investigators and by interlaboratory comparisons. In general, the methods are adequate when evaluated under carefully controlled laboratory conditions, but they yield marginally acceptable results when evaluated under round-robin (interlaboratory) conditions. Many of these procedures can be used to determine elemental chlorine in air by collecting the chlorine in absorbing solutions. The continued use of all these methods does not appear to be warranted. The use of *o*-tolidine methods should be discouraged, because the reagent itself is allegedly hazardous and because the methods are inferior to other methods. The use of N, N-diethyl-*p*-phenylenediamine (DPD) methods should be encouraged, because both titrimetric and colorimetric procedures for them exist, they have few interferences, and they are simple to use. The methyl orange colorimetric procedure is also attractive, particularly for analyzing absorbed impinger solutions. In recommending the adoption of these procedures, however, there is a danger that other--possibly superior--methods will not be given proper consideration. The leuco crystal violet procedure, for example, appears to be nearly ideal and should be evaluated thoroughly. Similarly, the barbituric acid procedure appears to perform well and should be studied further to establish its true utility.

In 1966, Gilbert suggested a means for flame-photometric determination of total chlorine. He modified a Van der Smissen burner to include indium, rather than copper, in its construction, so that the indium chloride spectral band would be emitted from the flame. The indium chloride band, which occurs at 359.9 nm, proved to be both selective and sensitive. For example, Gilbert estimated that about 0.001 μg of chlorine could be detected in 1 liter of air. The problem is that the detector would not be specific for chlorine or hydrogen chloride; it would respond to chlorine from any source. Nevertheless, the idea is intriguing and should be pursued as a possible means for source (and perhaps ambient) air and water monitoring.

Colorimetric procedures specific for hydrogen chloride are nonexistent. Electrochemical and gas-chromatographic methods have been studied, but have not gained wide popularity. Methods for determining hydrogen chloride, as opposed to total acidity or total chloride, are sorely needed. Electrochemical techniques that respond to H^+ and Cl^- already exist; they should be investigated jointly as a possible hydrogen chloride detector. Gas-chromatographic techniques are also known to work, but not satisfactorily enough to meet current needs. Research into increased inertness in chromatographic columns and into more sensitive and reliable detector systems is warranted. It has recently been reported that hydrogen chloride can be selectively and quantitatively absorbed from the gas phase by the phosphates of cadmium, zinc, mercury(II), and silver. This suggests the possibility of quantitatively collecting and concentrating hydrogen chloride specifically from the atmosphere before analysis. The use of a solid reactant as an absorber has obvious advantages over liquid absorbers. It might be combined with chromatographic or electrochemical measurement techniques to provide both specificity and extreme sensitivity. Research is warranted to understand and implement this phenomenon.

Simple tests that are reliable and reasonable in cost are needed. The development of simple and inexpensive monitoring instruments, particularly of the probe type, is needed. This is especially true of chlorine, because its samples are not stable over a long period. Research into the development of a chlorine-specific electrode is warranted. In fact, electrochemical monitoring devices of several types have been touted for some time, for both oxidizing and acidic constituents in water and air. Heretofore, instrumentation for these types of devices has been rather complex and expensive. Recent developments in instrumentation should allow inexpensive, compact, and simple electrochemical instrumentation to be developed for monitoring purposes. Modern electronic components and construction techniques should be used for air monitoring purposes for both chlorine and hydrogen chloride.

Methodology for generating standard gas mixtures containing known amounts of hydrogen chloride is needed for calibration purposes. Chlorine can be prepared in precisely known amounts by electrolysis and with permeation tubes, but these techniques are not suitable for preparation of gaseous mixtures of hydrogen chloride. Saltzman established that pure hydrogen chloride at 470 ppm could be swept reliably from 1:1 hydrochloric acid solution under carefully controlled conditions. This technique, although workable, is not suitable for general calibration purposes. New approaches to this difficult problem are needed.

APPENDIX: ANALYTIC DETERMINATION OF CHLORINE AND HYDROGEN CHLORIDE

This appendix deals with the analytic determination of elemental chlorine and vapor-phase hydrogen chloride. It is not concerned with the determination of total chlorine--i. e., with methods for determining total chloride ion--except for a few methods of particular interest because of their environmental utility or promise.

There are many more methods for determining molecular chlorine than there are for determining vapor-phase hydrogen chloride. Most methods for chlorine are based on its oxidative properties, whereas those for hydrogen chloride are based on its acidity. Accordingly, the two will be treated separately in the following discussion, except where it is particularly appropriate to discuss them together. Determinations of chlorine and hydrogen chloride in both aqueous and gaseous media are discussed in the following sections. The discussion is not oriented toward specific applications, but is oriented toward the analytic techniques and problems themselves. Many final measurements are common to both types of samples; only the sampling techniques differ.

The determination of chlorine in water is extremely important. It is used widely, both in the field and in the laboratory. A word about the terminology characteristic of this analysis is desirable. Chlorine in water is normally referred to as "available" or "active" chlorine. "Available" denotes availability for sterilization purposes; but for analytic purposes, it expresses iodine equivalency. Iodine equivalency is not necessarily analogous with ability to kill a particular species. Chlorine that is bound tightly in some organic compounds may not contribute to "available" chlorine. More importantly, chlorine in water may be combined with ammonia or other nitrogenous materials that also have oxidizing power, or it may be present as hypochlorite, OCl^-. The currently accepted terminology is as follows:

"Free available chlorine" (FAC), or "free available chlorine residual," refers to elemental chlorine, hypochlorous acid, hypochlorite ion, or all those acting jointly. "Combined available chlorine" (CAC), or "combined available chlorine residual," refers to the derivatives of ammonia or other nitrogenous compounds that have the capacity to combine with chlorine or hypochlorous acid so as to modify its rate of bactericidal action. Analytic procedures may distinguish FAC, CAC, and "total available chlorine" (TAC). Some procedures are even more selective and distinguish different species that fall within the category of CAC. Note that both free and combined available chlorine may be present simultaneously; they then constitute TAC.

In this appendix, "hydrogen chloride" will be used to refer to vapor-phase hydrogen chloride, and "hydrochloric acid" will be used to refer to hydrogen chloride in solution.

PROPERTIES OF CHLORINE AND HYDROGEN CHLORIDE PERTINENT TO CHEMICAL ANALYSIS

When dissolved in water, chlorine undergoes a small but measurable hydrolysis (disproportionation), according to the following reaction:

$$Cl_2 + H_2O \rightleftharpoons Cl^- + HOCl + H^+ \; ; \; K = 4.66 \times 10^{-4} .$$

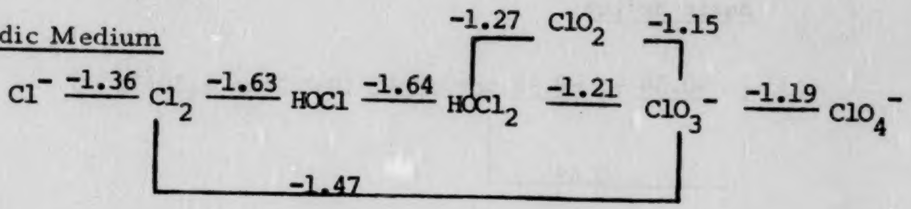
This reaction is rapid at the pH of natural waters. Only a low pH and at high chlorine concentrations does a measurable amount of molecular chlorine exist; hence methods for determining FAC actually determine both molecular chlorine and hypochlorite. The reaction can be made to go to virtual completion by adding a species that reacts with H^+ or Cl^- or both. For example, bicarbonate is too weak a base to react with hypochlorous acid, so its reaction with chlorine is as follows:

$$Cl_2 + HCO_3^- \quad Cl^- + HOCl + CO_2$$

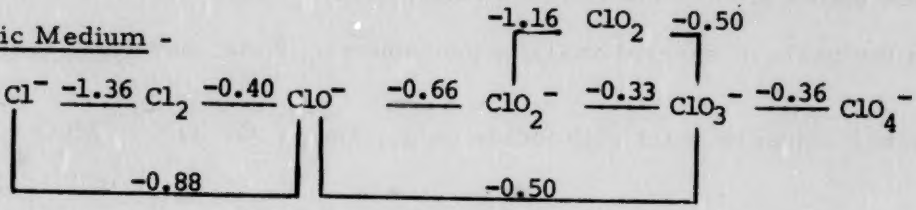
In strong base, hypochlorite salts are formed. Hypochlorous acid itself is weakly ionized ($K_a = 3.7 \times 10^{-8}$).

Aqueous oxidation potentials for the several chloro species are shown below:

Acidic Medium


-1.27
ClO2
-1.15
Cl-
-1.36
Cl2
-1.63
HOCl
-1.64
HOCl2
-1.21
ClO3-
-1.19
ClO4-
-1.47

Basic Medium -


-1.16
ClO2
-0.50
Cl-
-1.36
Cl2
-0.40
ClO-
-0.66
ClO2-
-0.33
ClO3-
-0.36
ClO4-
-0.88
-0.50

Hence, in acidic solution, hypochlorous acid and chlorous acid are thermodynamically unstable with respect to disproportionation, and chlorine and perchlorate are capable of oxidizing water. In basic solution, the only reaction that proceeds rapidly is the alkaline decomposition of chlorine. The standard aqueous oxidation potentials for iodinated species are also important, because of the role that iodine plays in the analytic chemistry of chlorine. They are as follows:

Acidic Medium

$$\begin{tikzcd}[column sep=large]
I^- \arrow[r, dash, "-0.54"] & I_2 \arrow[r, dash, "-1.45"] \arrow[d, dash] & HOI \arrow[r, dash, "-1.14"] & IO_3^- \arrow[r, dash, "-1.7"] \arrow[d, dash] & H_5IO_6 \\
 & {} \arrow[r, dash, "-1.06"] \arrow[d, dash] & ICl_2 \arrow[r, dash, "-1.23"] & {} \arrow[d, dash] & \\
 & {} \arrow[rr, dash, "-1.20"] & & {} &
\end{tikzcd}$$

Basic Medium

$$\begin{tikzcd}[column sep=large]
I^- \arrow[r, dash, "-0.54"] \arrow[d, dash] & I_2 \arrow[r, dash, "-0.45"] & IO^- \arrow[r, dash, "-0.14"] \arrow[d, dash] & IO_3^- \arrow[r, dash, "-0.7"] & H_3IO_6^{2-} \\
{} \arrow[rr, dash, "-0.49"] & & {} & &
\end{tikzcd}$$

At least thermodynamically, elemental chlorine and all positive oxidation states of chlorine can be quantitatively reduced by excess iodide. This is the basis of several analytic procedures. Note, however, that many other oxidants react with iodide (e.g., Cu^{2+}, $Cr_2O_7^{2-}$, MnO_4^-, Ce^{4+}), and many reducing agents can be oxidized by iodine (e.g., Sn^{2+}, SO_3^{2-}, H_3AsO_3). Moreover, chlorine itself reacts with iron, manganous manganese, nitrite, hydrogen sulfide, and a variety of organic materials. Accordingly, analytic procedures must be judiciously designed and carefully performed if accuracy is to be ensured.

In water that contains ammonia, a series of chlorine substitution reactions occur to form monochlorinated, dichlorinated, and trichlorinated species. These reactions deactivate chlorine, converting it ultimately to chloride, the products and rate depending heavily on pH. These reactions form the basis of the "breakpoint" chlorination procedure: chlorine is added to water that contains ammonia until the ammonia is consumed. Continued addition of chlorine after ammonia and amines are consumed yields "free" chlorine. This occurs after 3 moles of hypochlorous acid are added for each mole of ammonia. This explains the need for analytic procedures that distinguish different "forms" of chlorine. The situation is complicated from the analytic point of view, however, in that organic materials in water may react with chlorine slowly and may form tightly bound chlorinated derivatives that are not reactive or partially or slowly reactive to iodide. Thus, analytic results often are more empirical than the procedure might indicate.

Hypochlorous acid and hypochlorite are both unstable, especially in the presence of sunlight. Draley[111] reports that in sunlight it takes about 31 sec to reduce the concentration of free chlorine from 0.5 to 0.01 ppm. In the dark, an equal decrease may require 30 min to several hours. This susceptibility to light is especially important in designing sampling procedures and methods for field use. Monochloramines and dichloroamines are much more stable.[15]

SAMPLING

Chlorine in aqueous solution is not stable, and the chlorine content of samples or solutions, particularly weak solutions, decreases rapidly. Exposure to sunlight or other strong light or agitation accelerates the reduction of chlorine in such solutions. Therefore, it is mandatory that chlorine content be determined as soon as possible after sampling and that excessive light and agitation be avoided. Samples to be analyzed for chlorine should not be stored.

All glassware used for the determination of chlorine residual should be exposed to water containing residual chlorine at at least 10 ppm for 3 hr or more and then rinsed with chlorine-demand-free water before use. Owing to the rapidity with which this water may absorb some laboratory fumes, it should be examined for nitrites, chlorine, and reducing agents immediately before its use for determining chlorine at very low concentrations.

Chlorine-demand-free water is prepared by adding sufficient chlorine to distilled water to destroy ammonia. (The amount required will be about 10 times the amount of ammonia nitrogen present; an initial chlorine residual of more than 1 ppm is mandatory.) The chlorinated distilled water is allowed to stand overnight or longer; it is then exposed to direct sunlight until all residual chlorine is discharged. Irradiation with a bare ultraviolet light source is sometimes used. Alternatively, chlorine-demand-free water can be prepared by ion exchange. A 3-ft (91.4-cm) column approximately 2.5-5 cm in diameter containing both strongly acid cation-exchange and strongly basic anion-exchange resins is used. Distilled water is passed through this mixed-bed column at a relatively low rate and collected in a scrupulously clean receiver that is arranged to protect the treated water from exposure to the atmosphere. A sulfuric acid or calcium chloride trap on the air inlet to a stoppered storage bottle must be used. The water is withdrawn by glass siphon through the same stopper. Unless such precautions are taken, the water may very quickly absorb ammonia from the atmosphere. In using ion-exchange columns, care must be taken to ensure that all organic materials are washed from the resins before use, because even trace amounts of methylamine could destroy the integrity of chlorine-demand-free water. Because water used for preparation and dilution of samples and for rinsing glassware must also be free of elemental chlorine, the water should be checked for the absence of chlorine before use.

Collection of Air Samples

Air samples for chlorine and hydrogen chloride are collected either in absorber or impinger trains or in evacuated sampling bulbs (i.e., "grab" samples). Numerous arrangements have been devised to meet specific requirements. Typical sampling procedures and equipment are described elsewhere.[87, 88] The usual sampling train consists of two to four impingers or absorption vessels, a gas drying tube, a pump, and a flowmeter. Heated (250 C) sampling probes are included for stack sampling applications. All-glass construction minimizes corrosion and absorption losses. The usual grab sampler is a Pyrex bulb of known volume (e.g., 2 liters) fitted with a coarse probe-filter to remove particulate matter.

Absorption columns (bubblers) are preferred for longer-term (about 24-hr) sampling. The compact sampler developed for the National Air Sampling Network has proved to be reliable and easy to operate and maintain.[344] It consists of a bubbler connected through a filter and critical orifice to a pump. The in-line filter protects the critical orifice; a membrane prefilter removes particulate matter. Polypropylene centrifuge cones serve as absorption vessels, and plastic and Teflon components and fittings are incorporated for ruggedness. These trains are designed to operate from a manifold that accommodates five sampling units in parallel. The temperature of the samplers can be controlled at 35 C. Air flow typically is 150-200 cm^3/min at a vacuum of 16-20 in. Hg (406-508 mm Hg). These units were designed for sulfur dioxide and nitrogen dioxide measurements, but should be equally effective for chlorine and hydrogen chloride.

Several different absorber solutions are commonly used for chlorine and hydrogen chloride, depending on the particular application. Water or, preferably, dilute sodium hydroxide solution is used for hydrogen chloride. The solution can then be analyzed for acidity or for chloride content. Chlorine is commonly absorbed in standard sodium arsenite solution or in excess potassium iodide solution.[236] The solution can then be analyzed by determining excess arsenite or iodide or perhaps liberated iodine.

When both chlorine and hydrogen chloride are present, two analyses are required (chlorine and total chloride), so that hydrogen chloride can be determined by difference.

Meador and Bethea[337] compared the standard bubbler technique with glass- and polypropylene-syringe gas sampling techniques and found that the polypropylene syringe technique was superior for both chlorine and hydrogen chloride analysis in polluted air. They used disposable 50-ml polypropylene syringes that had been preconditioned by cleaning with acetone and then overnight exposure to the gas at several thousand parts per million. For chlorine determination, a minimal amount of liquid (3 ml) was placed in the syringe to absorb free chlorine from a 47-ml gas sample. The liquid contained o-tolidine at a concentration of 0.005 g/liter in 10% hydrogen chloride. Under these conditions, the lowest detectable concentration of chlorine was 0.12 ppm in air. The syringe was held above and nearly perpendicular to the gas sample line, so that chlorine bubbled through the o-tolidine reagent in the syringe and was immediately absorbed. Contact of free chlorine with the syringe walls was thus minimized. This was necessary, because free chlorine apparently was absorbed on the walls of the plastic syringe. Reproducibility was also enhanced by thoroughly rinsing the syringes with fresh reagent between samples. The relative error using the above technique was 3.4% at 4.0 ppm. Reproducibility was poorer when glass syringes were used.

The syringe technique was also used for determining hydrogen chloride in air. The colorimetric method of Iwasaki *et al.*[240] was used. This method measures total chloride, in that it is based on the reaction of chloride and mercuric thiocyanate and measurement of the reddish-orange color of ferric thiocyanate. Although the method was optimized for use with syringe sampling, Beer's law was not obeyed; thus, the calibration curves were nonlinear and of low slope. Hence, the relative errors for analysis of samples in this concentration region were high: 24.7% with hydrogen chloride at 30 ppm in air, 10% at 12 ppm, and 8% at 0-5 ppm. The lower detection limit of this method was found experimentally to be 0.5 ppm in air.

Continuous Monitoring

Chlorine and hydrogen chlorine have been monitored continuously both electrochemically and spectrophotometrically.

Chlorine in water has been monitored continuously by "coulometry."[125,462] In this approach, ferrous ions are generated electrolytically in an electrolytic cell. Any oxidant (such as chlorine) that enters the cell and reacts with ferrous ion is monitored by following the electrolytic current required to maintain a preselected ferrous concentration. Because electrolytic current is monitored, the technique is not truly coulometric, but rather is amperometric. The progress of the reaction is followed potentiometrically with a platinum-calomel electrode pair. If any difference develops between the detected potential and the preselected potential, then a current is generated that restores the system to its steady-state value. Such devices have been used for many years. They are characterized by accuracy (± 1% is typical) and by lack of specificity. Similar systems have been devised for several gaseous air pollutants, including chlorine. For example, the Detectachlor chlorine-gas leak detector, marketed by Fischer & Porter Co., is based on continuous amperometric monitoring of the ferrous-ferric couple in a solution saturated with sample air. The Chlorine Detector, marketed by Wallace & Tiernan Division of the Pennwalt Corporation, is similar, except that the iodide--iodine electrolytic couple is monitored, rather than the ferrous-ferric couple. Such instruments can detect chlorine in air at 1 ppm or above, so they are useful primarily as warning devices where release of chlorine gas is a possibility.

A simpler and more recent approach uses so-called ion-selective electrodes for measuring or monitoring chlorine in water. These are potentiometric devices that respond semilogarithmically to the concentration (i.e., activity) of the species being measured. No electrode is available that responds directly to molecular chlorine, but hypochlorite can be determined indirectly with an iodide-selective electrode.[369] This approach can be used for discrete samples or for continuous monitoring. The concentration range for good performance (± 10% accuracy) is 0.1-100 ppm, with a lower detection limit of 0.05 ppm. Response time of the monitoring system is 8-10 min (99% response to a stepped concentration change at the inlet). A marriage between this aqueous monitoring system and an absorbing sampler for gaseous samples seems attractive.

Potentiometric monitoring of gaseous constituents is not new. Lee[297] devised a continuous monitoring system for hydrogen chloride in gaseous mixtures that was based on the response of a chloride-selective electrode. The problem is that total chloride is not necessarily analogous to hydrogen chloride. More specificity could be achieved by monitoring both hydrogen ion and chloride potentiometrically in the absorber solution, using a pH electrode in parallel with a chloride electrode.

A somewhat similar approach for continuously monitoring hydrogen chloride in gaseous mixtures was recently reported by Brittan, Hanf, and Liebenberg.[53] They used an automatic (volumetric) titrator to neutralize hydrogen chloride continuously as it was absorbed from the gas stream, and titrant flow was recorded as a function of time. A glass-calomel electrode pair was the sensing system, with the selected pH set at 5, to avoid carbonate ion interference. Chlorides were trapped out of the heated sampling probe. The technique was suitable for determining gases that contained hydrogen chloride at 10 ppm to 20%.

A number of laboratory and continuous monitoring systems are marketed, all of which are based on spectral detection and measurement. The Technicon AutoAnalyzer is the most widely used automated system for wet chemical analysis. Most conventional wet chemical procedures are adaptable to the Technicon system, and they can be implemented for monitoring water or air.

The determination of chloride by indirect formation of ferric thiocyanate has been modified for AutoAnalyzer use for aqueous samples. Most of the spectrophotometric methods described in the following section could also be adapted for automated or continuous operation via the AutoAnalyzer approach.

Finally, it should be mentioned that there are physicochemical monitoring devices on the market that are not based on wet chemistry. Beckman Instruments, Inc., includes chlorine and hydrogen chloride monitors in its line of nondispersive analyzer systems. Chlorine is measured in the ultraviolet region; hydrogen chloride is determined in the infrared region. Both are sensitive enough (about 10 ppm) for monitoring for episodal situations, but insufficiently sensitive for ambient monitoring. This is true of chlorine and hydrogen chloride monitors in general. It points to a need for research into monitoring systems that afford roughly a thousandfold increase in sensitivity over existing devices.

ANALYSIS

Almost all analyses for chlorine in aqueous samples are titrimetric or colorimetric. The most common methods are listed in Table A-1. Most of the methods in Table A-1 are discussed in some detail in Standard Methods for the Examination of Water and Wastewater[467] and the Handbook of Chlorination.[514] They have been thoroughly tested and evaluated by numerous workers. The critique by Nicolson[361] is particularly thorough: three titrimetric and nine colorimetric methods are included. Table A-1 includes relative standard deviations and relative error values resulting from extensive testing of known samples by about 30 laboratories, as reported in Standard Methods. A larger study by the Analytical Reference Service[304] has also been conducted on a number of the methods in Table A-1, and the recommendations resulting from that study are listed as a separate entry--"ARS Study." It is clear from these

TABLE A-1

Common Analytic Methods for Chlorine[a]

Method	Determination[b]	Common Concentration Range	Common Interferences	Results of ARS Study[c]	Relative Standard Deviation, %	Relative Error, %
Iodometric titration (I_2 with S_2O_3)	TAC	More than 1 ppm (detection limit, 40 ppb)	Oxidants, reductants	Not tested	23-32	16-23
Amperometric titration (Cl_2 with phenylarsine oxide)	FAC CAC TAC	Less than 2 ppm	Br_2, I_2, Cu, Ag, NCI_2 ClO_2	Acceptable for TAC only	3.9; 12-42	8-25
DPD titration (Cl_2 with Fe^{2+})[d]	FAC CAC TAC	4 ppm	Br_2, I_2, Mn, NCI_3, ClO_2	Acceptable for FAC and TAC	4.5; 9-40	4-20
o-Tolidine; colorimetry	FAC CAC TAC	10-10,000 ppb	Fe, Mn, NO_2, ClO_2, Br_2, I_2, O_3	Not tested	3.0; 31-65	20-42
o-Tolidine-arsenite (OTA); colorimetry	FAC CAC	10-10,000 ppb	--	Unacceptable for FAC and TAC	28-52	14-49
Stabilized neutral o-tolidine (SNORT)	FAC CAC	10-6,000 ppb	--	Performed well; acceptable for FAC and TAC	3.7; 8-35	2-13

TABLE A-1 (continued)

Method	Determination[b]	Common Concentration Range	Common Interferences	Results of ARS Study[c]	Relative Standard Deviation, %	Relative Error, %
DPD; colorimetry	FAC CAC	0.1-2 ppb	Mn^{3+}	--	2.0	--
Leuco crystal violet; colorimetry	FAC TAC	10-2,000 ppb	Mn^{3+}	Excellent; Acceptable for FAC and TAC	1.8 32	1-18
Methyl orange; colorimetry	FAC TAC	100-2,000 ppb	Mn^{3+}, Br_2	Acceptable for FAC and TAC	20-43	7-22

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[a] Data from Bjorklund and Rand,[38] Lishka and McFarren,[304] Nicolson,[361] Palin,[370] Sollo and Larson,[444] Taras,[466] Taras *et al.*,[467] and White.[514]

[b] FAC = free available chlorine; CAC = combined available chlorine; TAC = total available chlorine.

[c] Ref. 304.

[d] DPD = N, N-diethyl-*p*-phenylenediamine.

data that the methods are inherently precise and accurate enough for most environmental needs, but in actual practice their performance is at best marginal. An important advantage of automated or continuous methods is that they minimize the human contribution.

Titrimetric and Colorimetric Techniques

The iodometric titrimetric method is considered the standard by which other methods are judged or on which they are based. Chlorine will liberate free iodine from potassium iodide solutions when their pH is 8 or less. The liberated iodine is titrated with standard sodium thiosulfate solution, usually using starch as the indicator. The reaction is preferably carried out at pH 3-4. This method provides the means for standardizing chlorine water used in preparing temporary standards for other methods. It is also suitable for the determination of high chlorine residuals. The iodometric method is generally more precise than colorimetric methods when the residual chlorine concentration exceeds 1 mg/liter, but it is not accurate at lower concentrations or in the presence of interferences. This procedure is particularly susceptible to interferences, inasmuch as both oxidants and reductants can cause errors. The standard potential of the iodide-iodine couple is such that many common species either oxidize iodide or are oxidized by iodine.

The amperometric titration method is largely unaffected by the presence of common oxidizing agents, temperature variations, turbidity, and color. The method is not as simple as colorimetric procedures and requires greater operational skill to obtain its inherent accuracy. In this method, FAC is titrated at a pH of 6.5-7.5 with standard phenylarsine oxide solution, and the progress of the titration is monitored amperometrically. This means that the titration is carried out in an electrolytic cell that is fitted with a platinum indicator electrode and a reference electrode, and the voltammetric current between these two electrodes is monitored. The voltammetric current acts as a null-point indicator, being large when the chlorine residual is high and decreasing to a minimum when the chlorine residual disappears. The end point is recognized when no further decrease in current can be obtained by adding more phenylarsine oxide. CAC can be determined by this procedure if potassium iodide is added and the titration repeated at a pH of 3.5-4.5. The Analytical Reference Service study[304] found the amperometric titration procedure to be acceptable only for the determination of TAC. The unacceptability of this procedure for determining FAC may be attributable to its need for strict pH control. It may also be due to the fact that stirring can lead to loss of chlorine via volatilization. It is noteworthy that other halogens (bromine and iodine) are titrated exactly like chlorine in this procedure. Copper and silver have also been identified as interferences. However, manganese, nitrite, and iron do not interfere, although they can be serious interferences in most of the other procedures listed in Table A-1.

The o-tolidine methods have gained wide acceptance for the routine measurement of residual chlorine in water, both industrially and in the field. The o-tolidine-arsenite (OTA) method permits the differentiation of FAC and CAC in the presence of color from common interfering substances. The OTA modification is satisfactory for routine control with properly calibrated photometers, visual color disks, or permanent color standards. The Analytical Reference Service study found the OTA method to be unacceptable for FAC and TAC. But the stabilized neutral o-tolidine (SNORT) modification performed well and was considered acceptable for both FAC and TAC.

o-Tolidine methods are based on the formation of the characteristic yellow halogen derivative that results from the reaction between chlorine and o-tolidine. Correct color development with chlorine is obtained when the solution pH is 1.3 or lower, the ratio by weight of o-tolidine to chlorine is at least 3:1, and the chlorine concentration does not exceed 10 ppm. The reaction time and temperature are critical in this procedure and must be controlled carefully to minimize loss of color by fading or increase of color due to interfering oxidizing agents. Such interferences include ferric and manganic ions and nitrites. The yellow holoquinone color obeys Beer's law over a considerable chlorine range. Samples that contain predominantly free chlorine are characterized by maximal color development almost instantly, and then the color begins to fade. Samples that contain combined chlorine develop the maximal color at a rate that depends largely on temperature: at 20 C, maximal color is developed in about 3 min. About 5 min after maximal color development, a slight fading begins. Therefore, samples containing combined chlorine should be read within about 5 min; color development preferably goes on in the dark. It must be emphasized that the precision of the results depends on strict adherence to the recommended intervals and the temperature of the sample.

The OTA method is designed for use whenever interferences--such as ferric and manganic ions, nitrites, and organoiron compounds--are suspected. However, according to the Analytical Reference Service study, the OTA procedure is unacceptable for FAC and TAC measurements. Because of the critical dependence on technique, this method is very likely to be in the category of methods that can be used satisfactorily by experienced personnel and can be disastrous in the hands of inexperienced personnel.

The SNORT modification performed well in the ARS study and is considered acceptable for FAC and TAC measurements. o-Tolidine has classically been used at a pH of 1. 3 or lower, because the stability of the oxidized form decreases as the pH increases. As the pH increases, however, the rates of reaction of o-tolidine with combined chlorine, iron, and nitrite become lower; their interfence essentially disappears at pH 7. The SNORT procedure capitalizes on this fact. Anionic surface-active agents stabilize the color developed by free chlorine and *o*-tolidine at a pH of 7. To ensure correct color development and minimal interference, a pH of 6.5-7.5 is specified and a ratio of *o*-tolidine to free chlorine of at least 8:1 is used. The sample must be added to the reagents. The reaction time and temperature are relatively unimportant in this procedure, compared with other procedures. Complete mixing of the sample and the reagents and reading of the absorbance are usually accomplished within 2 min. Potential interferences include bromine, chlorine dioxide, iodine, manganic compounds, and ozone. The reduced forms of these compounds do not interfere. It is to be emphasized that reducing agents like ferrous compounds, hydrogen sulfide, and oxidizable organic matter do not form an interference in the analytic method, but may interfere by reducing the chlorine residual by reaction with elemental chlorine. Although the SNORT method is still considered tentative in *Standard Methods*, it is clearly superior among the *o*-tolidine procedures. The use of permanent chlorine standards based on the color of carefully prepared chromate-dichromate solutions is advantageous. The use of standards based on the formation of the holoquinone derivative itself is problematic, because the color is not stable.

Because *o*-tolidine is regarded as a potential cause of tumors in the urinary tract, its use has been abandoned in the British Isles.[514] The only colorimetrtic method in use there is the N,N-diethyl-*p*-phenylenediamine (DPD) method. FAC reacts instantly with DPD to produce a red color. This reaction is the basis of both titrimetric and colorimetric procedures. In the titrimetric procedure, the FAC is titrated with standard ferrous ammonium sulfate solution to the disappearance of red. The decolorization is instantaneous. In the colorimetric version of this method, standard colors are prepared with a standard potassium permanganate solution and compared with colors formed by the reaction with free elemental chlorine. The colors are stable, few reagents are required, and a full response in neutral solution is obtained from dichloroamine. The only interfering substance likely to be encountered in water is manganic manganese. This can be corrected for by including sodium arsenite in the test portion. The DPD colorimetric procedure has been studied extensively by Bjorklund and Rand.[38] The titrimetric procedure also was included in the Analytical Reference Service study and found to be acceptable for both FAC and TAC. A. T. Palin, to whom this method is attributed, has also published a modification of the procedure that is of particular utility for field use.[370] In this modification, the reagents are available in table form; hence, the procedure is both simple and rapid.

The compound 4, 4', 4''-methylidyne-tris (N, N-dimethylaniline), also known as leuco crystal violet, reacts instantaneously with free chlorine to form a bluish color. If this reaction is carried out in a buffered medium at a pH of 3.6-4.3, if the ratio of leuco crystal violet to chlorine is at least 30:1, and if the color is measured within 5 min, the reaction can be the basis of a colorimetric method for both FAC and TAC. No significant interference from CAC occurs when the free chlorine content is determined within 5 min after indicator addition. The one interference that deserves attention in the determination of free residual chlorine is manganic ion, and it may be overcome by addition of arsenite, as in the OTA method. TAC is measured by reacting both free and combined chlorine with iodide ion to produce hypoiodous acid, which in turn reacts instantaneously with leuco crystal violet to form the dye crystal violet. The color is stable for days and follows Beer's law over a wide range of total chlorine values. Semipermanent color standards for TAC determination can be prepared from the crystal violet itself. The minimal detectable concentrations are 10 ppb for FAC and 5 ppb for TAC. The Analytical Reference Service study found this method to be excellent and acceptable for FAC and TAC, but its findings were qualified by the fact that relatively few laboratories participating in the study used this procedure. The leuco crystal violet method has almost ideal characteristics; its use should increase.

At a pH below 3, methyl orange is red and has an absorption spectrum that exhibits a maximum at 510 nm. Chlorine bleaches that color quantitatively. Accordingly, if the change in absorption is measured, the concentration of free chlorine in a solution added to a known amount of methyl orange may be established. At a pH of 2 or greater, the rate of reaction of chloroamines with methyl orange is very low; but in the presence of excess bromide ion, chloroamines also bleach methyl orange rapidly. Therefore, sodium bromide may be added to the sample after the free chlorine concentration is determined, and the additional decrease in absorption will be due to chloroamines. This method was found to be acceptable for FAC and TAC in the Analytical Reference Service study, and it has also been evaluated thoroughly by Sollo and Larson.[444] The methyl orange method has been adopted as a "tentative" method by the Intersociety Committee for a Manual of Methods of Air Sampling and Analysis for determining free chlorine in the atmosphere.[470] The method has some advantages: it is simple and quick and can be run visually; the reagent serves as its own standard and so can be used for both routine and occasional use; manganic manganese is the only interference, and it can be removed by the arsenite modification; the method is sensitive to chlorine at 100 ppb; and it is independent of sample temperature. The major disadvantage is that the method is based on bleaching, rather than formation, of a color. This means that precise addition of reagents is required, and it also lends something of a credibility gap to the procedure: one always wonders whether the bleaching is truly due to the reactant of interest.

A method that is not commonly used in the United States, but performed especially well in Nicolson's study,[361] is the barbituric acid method.[13] It is based on the formation of a red-violet complex when an aqueous chlorine-potassium cyanide solution is mixed with an aqueous solution containing pyridine and barbituric acid. At the absorption maximum of 578 nm, Beer's law is obeyed over a wide concentration range--1-2,500 ppb. This method is not as simple to perform as most other colorimetric methods for FAC, and in time it responds to combined chlorine; the latter probably accounts for its disfavor in the United States. It was, however, rated by Nicolson as the best method for determining FAC.

There are no colorimetric procedures that determine hydrogen chloride as such. The Iwasaki _et_ _al_. method[240] was developed originally to meet the need for a procedure for measuring small quantities of chloride in natural waters. The method is based on the reaction of chloride ion with mercuric thiocyanate to form mercuric chloride, tetrachloromercurate-II, and thiocyanate. The orange color of ferric thiocyanate is measured at 490 nm as an indirect indication of chloride. When dioxane is included in the test portion, the absorbance-concentration relationship obeys Beer's law and can be used over the chloride concentration range of 0.05-80 ppm. The problem with this procedure is that any substance that reacts with mercuric thiocyanate to liberate thiocyanate will falsely indicate chloride. Sulfide is a prime example of interference for environmental applications. Turbidimetric and nephelometric methods that are based directly or indirectly on the formation of silver chloride have a similar disadvantage. Again, these methods determine chloride, not hydrogen chloride.

The other approach to colorimetric analysis for hydrogen chloride utilizes hydrogen ion response. Manita and Melekhina, for example, have reported a spectrophotometric method for the determination of nitric and hydrochloric acids in the atmosphere.[318] Their procedure is simple; it is based on the color of an ethanolic solution of methyl red when it contacts dilute hydrochloric acid solution. The maximal wavelength for this measurement is 530 nm, with distilled water as the blank. Under the proper conditions, there is a linear relationship between absorbance and acid concentration at 0.18-1.83 ppm. For the determination of acids in atmospheric air, a sample of air was passed through 5 ml of distilled water at 1 liter/min; samples of 10-20 liters were collected and measured spectrophotometrically. These workers showed experimentally that, under their conditions of sampling, carbon dioxide and sulfur dioxide in the air did not interfere with the spectrophotometric determination of hydrochloric or nitric acid. However, other acidic and basic constituents do interfere in this procedure. The standardization for this method was based on the use of hydrochloric acid solutions, so the method conceivably could be used for measuring dilute aqueous samples of hydrogen chloride; but the method obviously has little specificity and would be subject to great interferences from acidic and basic constituents in the sample.

The Intersociety Committee for a Manual of Methods of Air Sampling and Analysis endorses a titrimetric procedure for determining the chloride content of the atmosphere.[471] It is based on the formation of mercuric chloride; chloride in an absorber or impinger solution is titrated with mercuric nitrate, with diphenylcarbazone as the indicator. A blue-violet color is developed as soon as excess mercuric ion is added. Steps are taken to circumvent interference from chromates, ferric iron, sulfite, and sulfide; but iodide, bromide, cyanide, and thiocyanate are titrated and reported as chloride. The procedure is designed to determine 0.1 mg of chloride in 50 ml of solution (2 ppm), with an error of up to 0.1 ppm or 2%, whichever is greater.

Electrochemical Techniques

The determination of chlorine in water and sewage samples has been studied briefly by conventional voltammetric techniques with a silicone-graphite electrode.[387] The supporting electrolyte used in these studies was 0.1 N sulfuric acid. The electrode reaction in unstirred solution gave an exemplary waveform for an irreversible process at a stationary electrode, with the peak potential occurring at about +0.3 V vs. the saturated calomel electrode (SCE). Although the electrode reaction was shown to be irreversible, it was useful for the determination of chlorine at 10^{-3}-10^{-2} M. Peak height was measured and found to be linearly related to concentration over that range. With stirred solutions, satisfactory calibration curves were obtained at 10^{-4}-10^{-3} M.

Work at the Oak Ridge National Laboratory has shown that the reversibility of the chloride-chlorine couple depends strongly on sulfuric acid concentration. The couple becomes reversible at sulfuric acid concentrations of about 6 M and above. This means that chlorine can be determined by electrolytic reduction, and chloride can be determined by electrolytic oxidation in 6 M sulfuric acid at a platinum working electrode. The formal potential under these conditions is about +1.0 V vs. SCE. This approach is being developed specifically for air monitoring. It could easily be developed for water monitoring.

Kuempel and Shults[285] studied the use of a mercury pool electrode for measuring chlorine in air. They used a thin-layer cell configuration and two techniques of measurement: a controlled-potential experiment in which molecular chlorine was reduced to chloride with 100% current efficiency, the electrolytic current being monitored, and electrolytic accumulation of solid mercurous chloride at the mercury solution interface followed by stripping of the accumulate calomel voltammetrically. The amount of electric charge transferred during the voltammetric stripping (i.e., the area under the current-voltage curve) was related to the amount of chlorine in the air during the accumulation step. Concentrations of chlorine in air of 100-200 ppb were measurable.

J. Waolavik and Waszak[501] studied a galvanic system for measuring chlorine in air. It used a gold electrode paired against an active silver electrode in a closed system. A supporting electrolyte composed of potassium chloride solution acidified with hydrochloric acid was circulated in a closed system. The determination of chlorine bubbling through this electrolyte was based on the reduction of chlorine to chloride at the gold electrode; the silver electrode was oxidized to silver chloride. The galvanic current was measured directly without amplification, and its magnitude reflected the presence of chlorine and was proportional to its concentration. This approach is simple and allows rapid determination of small quantities of chlorine in gases. The technique allowed the determination of chlorine at 1.5 ppm with an accuracy of 0.02 ppm.

In contrast with these methods, which require complete dissolution of the active gas in water containing a suitable supporting electrolyte before the electroanalytic measurement is made, Cante et al.[65] reported the detection and determination of acid vapors at partially exposed platinum electrodes. The principal feature of their cell is a partially exposed sensing electrode that permits the gaseous sample to react without prior dissolution of the vapor in the bulk electrolyte. This absorption-induced electrode-potential approach was used to detect acidic vapors via the reaction:

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O.$$

This reaction does not take place in neutral or alkaline medium, and it is very sensitive to hydrogen ion concentration. Hence, the electrolytic cell is set up as follows: Pt (exposed blade)Iodate, Iodide/Pt (immersed wire). Acidic vapors are injected into a nitrogen stream that flows continuously through the cell. On entering the cell, the vapor is absorbed into the electrolyte meniscus at the exposed electrode, where active components react chemically with the electrolyte to produce iodine. The cell functions amperometrically, with the magnitude of the current response being proportional to the concentration of iodine (depolarizer) in the cell electrolyte. The current is proportional to iodine and hence to hydrogen ion, because the two are related stoichiometrically. A linear relationship between the limiting current for iodine and moles of hydrochloric acid injected was observed over the acid concentration of $1\text{-}7 \times 10^{-5}$ M. This approach, although interesting, does not offer selectivity: it would respond to both strong and weak acids in the air stream.

Finally, potentiometric measurements with ion-selective electrodes should be mentioned. The determinations of FAC in water[369] and of chloride in gas streams[297] by this approach were mentioned earlier. Because of their simplicity and rather selective response, ion-selective electrodes appear to offer promise of environmental analysis for chlorine and chloride. This promise is just beginning to be developed. It is likely that an electrode could be designed that responds to chlorine, and perhaps to hydrogen chloride, directly. Research in this area is warranted.

Chromatographic Techniques

In view of the success that gas chromatography has had in the determination of some constituents (e.g., sulfur dioxide) in air, it is surprising that there have been so few reports of the application of this technique to the determination of chlorine and hydrogen chloride in air. Myers and Putnam found gas-chromatographic conditions suitable for the determination of hydrogen chloride in their study of chloroboranes and diboranes.[352] They were able, by use of Teflon, Fluorolube, and silicone columns and by operating under subambient conditions, to separate hydrogen chloride from other constituents in their samples. Their procedure was not extremely sensitive--they were detecting mole percentages of hydrogen chloride but it did suggest the potential of this technique for monitoring air. The most successful design used a 10-ft (3-M) length of 1/4-in. (0.635-cm) OD copper tubing filled with 42-60 mesh uncoated Teflon powder. Hydrogen chloride values in the range of 0.01-5.0 mole % were determined by peak height measurements.

Both chlorine and hydrogen chloride were included in a broad chromatographic study of Bethea and Meador.[34] This work was a study of chromatographic conditions suitable for use with many reactive gases. They found suitable conditions for separating and detecting chlorine and hydrogen chloride, but their work was qualitative, rather than quantitative. The lower detection limit of 0.3 ppm for chlorine in air was reported when 1-ml samples and an electron-capture detector was used. The relative analysis error was ± 10% for chlorine at 10 ppm under these conditions.

Ceiplinski[71] found that 3×10^{-12} g of chlorine could be detected in a 50-µl air sample with a 1-m column packed with 20 wt % silicone fluid DC-200 on 60-80 mesh Chromosorb W at 50 C. The carrier gas in this case was 1% methane in argon and an electron-capture detector was used. Obermiller and Charlier[364] achieved quantitative separation of a mixture of hydrogen sulfide, hydrogen chloride, and water at 90 C with 5%

Carbowax 20 M on a Fluoropak support. The lower detection limit for hydrogen chloride was 0.1% with a 1-ml sample. Helium was the carrier gas. It was necessary to precondition this column with 5 ml of hydrogen chloride before analysis of any samples; otherwise, results were invariably low. Hamlin, Iveson, and Phillips[188] used a 14-ft (4.3-m) column packed with 16.7% Kel-F 40 oil on Kel-F 300 low-density molding powder at 90 C for the separation of chlorine and hydrogen chloride in the presence of reactive inorganic fluorides. Nitrogen carrier gas was used at a flow rate of 10 ml min.

Perhaps the most successful chromatographic analysis for chlorine and hydrogen chloride in air was reported by Ruthven and Kenney.[406] They used a tritolylphosphate column supported on Celite. This stationary phase was advantageous, in that the normal order of elution is reversed--i.e., chlorine is eluted before hydrogen chloride. The chlorine peak was therefore unaffected by tailing in the hydrogen chloride peak. The column was as follows: 220 cm of 3-mm ID PTFE tubing packed with 60-80 mesh acid-washed Celite having a liquid loading of 4% by weight of tritolylphosphate. The column was operated at room temperature. Chlorine gave sharp peaks with very little tailing, and the calibration proved to be linear with peak height. The relative accuracy and reproducibility for chlorine were estimated to be within 0.25%. However, the hydrogen chloride peak exhibited considerable tailing, especially when traces of moisture were present. Calibration with peak heights was nonlinear, but calibration based on peak area was found to be close to linear. Even so, hydrogen chloride could not be determined to the same degree of accuracy as chlorine: the minimal amount that could be detected was about 2%, and the accuracy was within 1-2%. Again, a column conditioning preface was mandatory for determining hydrogen chloride by this procedure. The time required for a complete analysis in this particular case was 1-2 min.

It is evident that gas chromatography has never gained acceptance as a routine analytic technique for chlorine or hydrogen chloride. The compounds can be separated and detected without sophisticated equipment, such as temperature programers or even heated columns. Unfortunately, the approach is thus far limited in sensitivity and in ease of quantitation. The attractiveness of this technique has not decreased, however; it responds to the molecular species themselves and hence offers specificity. In view of this and the fact that new materials and equipment are continually appearing, further research in the gas chromatography of chlorine and hydrogen chloride specifically is warranted.

Other Analytic Techniques

In much environmental work, there is a need for measuring total chlorine content by means other than wet-chemical techniques. Biologic materials, for example, may lose some or all of their chlorine by thermal ashing above 400 C. The same is true when tissues are ashed at low temperature with active oxygen. Analytic procedures that use fresh or dry tissue are required. Similarly, nondestructive analysis of particulate matter is desirable. X-ray fluorescence and neutron-activation analysis have been used for this type of application. These are expensive and sophisticated analytic techniques that provide multielement results. It is this multielement capability that makes them competitive for environmental applications.

X-ray fluorescence has been used for determining total chlorine content of biologic materials.[4] The tissues were lyophilized, ground to a fine powder, and mounted for excitation and measurement of the chlorine K_α radiation. Approximately 20 mg of sample is required: the calibration curve covers 0.4-5% chlorine. The results obtained by this technique were reproducible to ± 4%, with irradiations of only 3 min. Current x-ray fluorescence techniques offer the possibility of improving the sensitivity of this analysis by at least a factor of 100.

Neutron-activation analysis provides a direct method for the analysis of trace elements in airborne particulate material collected on filters, as well as biologic materials.[271, 382] The technique is characterized by extreme sensitivity and, when combined with γ-ray spectrometry, provides results for a number of elements simultaneously, without resort to chemical separation procedures. Computer interpretation of the γ-ray spectra makes the method suitable for routine application. Chlorine is determined via the ^{37}Cl(n,γ)^{38}Cl reaction, using particulate matter collected directly on filter paper as the specimen. The chlorine-38 decays with a characteristic half-life of 37.3 min, yielding prominent γ rays of 1.64 and 2.17 MeV. This procedure has been used to measure chlorine concentrations of 0.02-5.6 $\mu g/m^3$. Similar results for 17 other elements were obtained simultaneously in this study.[382]

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